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ANALYTICAL CHEMISTRY

A SERIES OF

LABORATORY EXERCISES

CONSTITUTING A PRELIMINARY COURSE OF QUALITATIVE
CHEMICAL ANALYSIS

COMPILED FOR THE USE OF BEGINNERS IN HIS LABORATORY

BY

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W. & R. CHAMBERS
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PREFACE.

THERE is no need to expatiate here on the aim of such a simple volume as this. Suffice it to state that the little book is a laboratory book, even in the sense that it has been written virtually in the laboratory, and in direct response to its wants. It has been used here in one form or another for upwards of a year. With the 'Practical Medical' and 'Practical Evening Classes' it serves us as *the* text-book on the subject; with the 'laboratory student' proper, as an introduction to my 'Manual of Analysis.' The little book has thus had the benefit of being tested by experience before publication, and I may say that it has stood the test well, and been of great service. I trust it will prove equally useful to those of my *confrères* who may adopt it as a text-book.

To my demonstrators and some friends I am indebted for the elimination of several slips that had crept into the 'original copy,' and for the introduction of some valuable amendments.

The book is not expressly intended for self-tuition; but, through the unqualified directness of its teaching, I hope it will satisfy the wants of even such students as only occasionally enjoy the benefit of the advice of an expert.

W. D.

ANDERSON'S COLLEGE,
September 1879.

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ANALYTICAL CHEMISTRY.

EXERCISES IN ULTIMATE ANALYSIS BY DRY-WAY TESTS.

Elements eliminated by Heat, and recognised by their Properties.

1. PLACE a small quantity of *mercuric* oxide, HgO, in the bottom of a 'sublimation-tube' (a tube of hard glass, closed at one end, about four inches long and a quarter-inch wide), and heat it. The compound will break up into oxygen, which escapes, and into vapour of metallic *mercury*, which condenses, in the colder portions of the tube, into metallic globules, liquid even at ordinary temperatures.

2. Place a small fragment of *iodine* in a sublimation-tube, and heat it gently in a gas-flame. The iodine is volatilised and changed into an intensely violet vapour, which, in the upper parts of the tube, will be condensed again into a solid, identical with the original substance.

3. Heat some *iodic anhydride* (I_2O_5) in a (not too narrow) test-tube. Violet vapours of iodine make their appearance and condense in the colder parts of the tube, while, at the same time, oxygen is liberated, which can be recognised by its property of inflaming a glowing splinter of wood.

4. Make a loop at the end of a thin platinum wire; heat this loop in the flame of a Bunsen's lamp, and dip it, quickly, into some powdered *carbonate of sodium* (Na_2CO_3),

when some of the salt will adhere to it. Heat the salt in the outer portions of the flame; it first melts, and is then gradually volatilised; the vapours are decomposed with formation of *metallic sodium*, which imparts to the flame an intensely yellow colour. When viewed through an ordinary laboratory spectroscope, the flame is found to give a spectrum consisting of one bright yellow line. The sodium vapours formed in this experiment cannot be condensed and collected; yet the *one* physical property referred to is sufficient to identify the metal with perfect certainty. What is here stated for carbonate of sodium holds good also for most of the other salts of this metal.

5. Repeat exercise, sect. 4; substituting for carbonate of sodium, successively, a salt of

a	*b*	*c*	*d*	*e*
Lithium	Potassium	Strontium[*]	Barium[*]	Thallium

Convenient salts for this purpose are, respectively, the

Carbonate	Carbonate	Sulphate	Chloride	Chloride

In each case the flame will assume a colour characteristic of the *metal;* the colours are, respectively,

Crimson	Violet	Crimson	Yellowish green	Pure green

Examine each flame with the spectroscope, and satisfy yourself that the spectra agree with the diagrams in the handbooks of Chemistry.

6. Heat, in a sublimation-tube, a small fragment of *arsenicum.* It volatilises without previously fusing, and the vapours condense into a ring-shaped metallic-looking sublimate, firmly adhering to the glass (a 'mirror').

Application of Heat and Reagents.

7. Place a fragment of *white arsenic* (arsenious anhydride, As_2O_3), about half the size of a pin's head, in the bottom of a sublimation-tube, previously drawn out into a narrow tail about two centimetres long and two millimetres wide; drop

---

[*] In the case of Barium and Strontium, a *hair-fine* platinum wire must be used, in order to maintain a temperature sufficient for the volatilisation of the compound.

into the tube a splinter of recently ignited charcoal shaped so as to stop up the conical part of the tube; and heat, first the charcoal until it is red-hot, and then the arsenic so that its vapours are driven through the red-hot charcoal. The charcoal, substantially consisting of carbon, C, takes away the oxygen of the compound, and the liberated metallic arsenic is deposited at some distance above the charcoal in the form of a mirror precisely similar to the one produced in exercise, sect. 6.

8. Heat a small quantity of *calomel* (HgCl) in a sublimation-tube. It is volatilised, and yields a sublimate identical with the original substance.

9. Heat, in a sublimation-tube, a mixture of *calomel* with about three times its bulk of *carbonate of sodium*. A sublimate of metallic mercury is produced (comp. sect. 1). The chlorine of the calomel remains in the residue as chloride of sodium.

10. Fuse on the end of a platinum wire, which has been previously bent into a loop (comp. exercise, sect. 4), a small quantity of *borax*, and heat the salt until it becomes a transparent colourless globule ('a borax bead'). Place on this bead a very little *binoxide of manganese* (MnO_2), and then expose it to the very tip of a blow-pipe flame containing an *excess of air* (an 'oxidising flame.' Such a flame is produced by placing the nozzle of the blow-pipe deep into the gas-flame, and then blowing rather hard, so that a non-luminous conical flame is produced; *only* the tip of the flame is *sure* to contain an excess of oxygen). The oxide of manganese dissolves in the borax and forms a bead, which, after cooling, appears violet, the colour being due to a compound of boracic acid, Bo_2O_3 with the oxide Mn_2O_3. Now heat the bead in a reducing flame, taking care that the bead is entirely enveloped in the flame. By a 'reducing flame' is understood a flame containing an excess of combustible gas, that is, more gas than can be burned by the air in it. As long as a blow-pipe flame is luminous, however slightly, it has reducing properties. If heated in this manner for a sufficient time, the bead, after cooling, appears *colourless*, containing now a compound of boracic

acid with the oxide MnO. The bead, when again heated in an oxidising flame, reassumes its original violet colour, and may then be decolourised again by a reducing flame, and so on.

11. Repeat this exercise, substituting successively oxides of the metals to be named for binoxide of manganese. The effects will be as follows:

	COLOUR OF BORAX BEAD WHEN PRODUCED IN	
	THE OXIDISING FLAME.	THE REDUCING FLAME.
Cobalt................	Intensely blue.	Intensely blue.
Chromium..........	Emerald green.	Emerald green.
Molybdenum.......	Yellow in the heat; colourless when cold.	Dark brown.
Nickel...............	Reddish, very faint after cooling.	Gray from finely divided reduced metal. On continued blowing, the metal agglomerates, leaving a clear bead.*
Iron..................	Hot: yellow. Cold: colourless or pale yellow.	Bottle green.
Copper.............	Green; after cooling, blue.	Brown - red, and opaque.*

12. Mix a few centigrams (say about twice the size of a pin's head) of *oxide of copper* (CuO) with two or three times its bulk of *carbonate of sodium*, and heat the mixture on charcoal by means of a *blow-pipe* in a *reducing flame*. After some minutes' heating, break off the fused mass along with those parts of the charcoal which are impregnated with the 'flux,' and triturate the whole in an agate mortar, first with one drop of water, then with more, and lastly, pour off all that does not readily subside in the water. Small flattened particles of metallic copper will be obtained, possessing the characteristic colour of that metal.

13. Repeat exercise, sect. 12, with oxide of *iron*, or oxide of *cobalt*, or oxide of *nickel* instead of the copper compound. You will obtain the respective metal in the shape of a

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* The reduction succeeds best on addition of some oxide of tin.

heavy gray powder, devoid, on account of its relative infusibility, of metallic lustre, but endowed with the property, characteristic of the *three* metals, of being attracted by a magnet. When brought into contact with a magnetised penknife, the metallic particles stick to it so that they can be lifted out of the mortar as a coherent lump. To shew that it is not the water which cements the particles of metal together, dry them at a gentle heat over a gas-flame, then remove them from the blade by letting the latter pass through between your thumb and forefinger, and then again touch them with the point of the knife. They will rise up and stick to it and one another, forming a beard-like cluster of filaments. This property of being attracted by a magnet combines iron, nickel, and cobalt into a genus, and enables them to be distinguished from all other metals. How the three metals may be distinguished from one another was shewn in Exercise 11. The finely-divided metals, when heated in a borax bead by means of an oxidising flame, soon pass into the condition of oxides, or rather borates.

14. Repeat Exercise 12 with *oxide of antimony*, Sb_2O_3, instead of oxide of copper. Metallic antimony will be produced, and in the elutriation process be obtained as a heavy metallic powder (the metal being very brittle). But as antimony is volatile at a red-heat, a considerable portion of the reduced metal volatilises, and in passing through the flame gets oxidised into Sb_2O_3, of which a portion is deposited on the charcoal as a white crystalline oxide ring. By continued blowing, the whole of the antimony can be volatilised in a short time.

Note.—Of other metals which, like those treated of in the last three exercises, are liberated from their oxides by the operation illustrated, the following may be named:

15. (1) *Zinc, Cadmium.*—These are completely volatilised, with formation of abundant oxide films. In the case of *zinc*, the film (ZnO) is yellow in the heat, but white after cooling. When moistened with *cobalt solution* and heated strongly, it is converted into a compound which, *after cooling*, is intensely green. *Cadmium:* the film (CdO) is brown.

16. (2) *Lead, Bismuth, Tin.*—These, being easily fusible, are (as a rule) obtained as 'beads.' A small portion of the metal volatilises with formation of a film. In the case of

	Pb.	Bi.	Sn.
The bead is......	Ductile.	Brittle.	Ductile.
The film is.......	Yellow.		White.*

17. (3) *Silver, Gold.*—These behave pretty much like copper. Obtained by elutriation as 'scales,' which in the case of

	Silver.	Gold.
Are...............	White.	Yellow.
There is.........	Hardly any	No
	Oxide film.	

18. (4) *Platinum:* obtained by elutriation as an infusible, heavy, *non-magnetic* powder. No film.

19. Take a few centigrams of *sulphate of baryta*, $BaSO_4$, mix it with carbonate of soda, and heat the mixture on charcoal as shewn (for CuO) in Exercise 12. The sulphate is reduced with formation of (carbonate of baryta and) sulphide of sodium, and hence the fused mass, when placed on a *silver coin* and moistened with a drop of water, produces a dark-brown stain of a sulphide of the coin-metal. This test applies to *all* non-volatile sulphur compounds.

Atmospheric or other Oxygen as a Reagent.

20. Take a small fragment of iron pyrites (FeS_2), and heat it in a *draught-tube* held slantingly over a Bunsen, so that the substance while being heated is exposed to a slow current of air. A part of the sulphur of the ore burns into sulphurous-acid gas, SO_2, which is recognised by its characteristic smell.

This is another sulphur test which, however, applies only to *metallic sulphides*, and is not absolutely general even for these.

21. Repeat exercise, sect. 20, with a fragment of (native) *arsenide of nickel* instead of the pyrites. Part of the arsenic of the ore is oxidised into arsenious acid, As_2O_3,

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* Becomes bluish green when heated with cobalt-solution.

which volatilises and condenses in the colder parts of the tube in the form of a characteristic-looking sparkling crystalline sublimate (which may be identified as shewn in sect. 7). This test applies to a vast number of other heavy-metallic arsenides.

22. Produce a carbonate of soda bead on a platinum wire, and next observe its appearance, (*a*) in the heat, (*b*) in the cold. Then attach to the bead a few milligrams of any *oxide of manganese*, heat the whole in the *oxidising* flame for a few minutes, and allow *to cool completely*. The bead now —containing the manganese as manganate, MnO_3Na_2O— exhibits a very intense and characteristic bluish-green colour.

This test applies to all non-volatile manganese compounds without exception.

23. Apply the operation illustrated in 22 to *oxide of chromium*, Cr_2O_3, taking care, however, to add a little nitrate of potash to promote the process of oxidation. The bead produced, containing the chromium now as alkaline chromate, K_2OCrO_3, exhibits a characteristic yellow colour, and when treated with a few drops of water (in a watch-glass) yields a still more intensely yellow solution.

This is a perfectly general test for all non-volatile chromium compounds.

24. After these exercises a number of lessons should be devoted to a practical examination, in which the student receives a series of unknown substances (selected so that something regarding their nature can be learned by means of the methods which he has become acquainted with), and is directed to report on each in writing, according to the following schema:

(1) Observations on colour and other general properties.

(2) Behaviour of substance when heated (*a*) by itself in sublimation-tube; (*b*) on platinum wire in a Bunsen's flame; (*c*) on charcoal; (*d*) in draught-tube.

(3) Behaviour of substance when heated with carbonate of soda (*a*) on charcoal; (*b*) on platinum wire.

(4) Colour of borax bead.

EXERCISES ON SALT REACTIONS.

REACTIONS OF THE ORDINARY MINERAL ACIDS AND 'CAUSTIC' BASES.

Sulphuric Acid.

(*a*) *Its Properties.*

25. Procure a supply of *pure oil of vitriol* (which may be taken as consisting of H_2SO_4), and observe: Its oily consistence; its high specific gravity; its high boiling-point (by heating a few drops in a test-tube); the thick heavy clouds formed when its vapour is produced in air (by volatilising one drop on platinum foil); its charring action on wood or cane-sugar; its violent action on water.

26. Place about 10 c.c. of dilute sulphuric acid in a beaker, colour it red with litmus solution, and then add, drop by drop, of a solution of caustic soda, NaHO, with continuous stirring, until the acid reaction is just destroyed, and no more.

Repeat the experiment, using litmus-paper (instead of litmus solution) as an indicator.

27. Saturate dilute sulphuric acid in a beaker with solution of carbonate of potash (or soda), K_2CO_3 (or Na_2CO_3), in two ways—namely, first, by adding the acid to the alkali in the cold until the CO_2 begins to come off freely, and then finishing in the heat; and secondly, by adding the alkali to the acid—finishing in the heat as in the first case.

28. Place in separate test-tubes small quantities of (*a*) chloride of sodium, NaCl; (*b*) nitrate of potash, KNO_3; (*c*) acetate of soda (we mean the salts themselves, not solutions); add to each a few cubic centimetres of oil of vitriol, and observe the effect, first without, and then with, application of heat. In each case the respective acid—in (*a*) HCl; in (*b*) HNO_3; in (*c*) $H(C_2H_3O_2)$—being more volatile than sulphuric, will be set free as a vapour. Report your observations; explain the several reactions by equations,

and formulate the general principles which you think are meant to be illustrated. You will readily understand that the effects produced by the vitriol are owing simply to its being a strong, and relatively non-volatile acid. The following exercises illustrate *specific* properties of the acid :

(*b*) *Reactions of Sulphates.*

29. Saturate dilute sulphuric acid with *baryta water* [solution of $Ba(OH)_2$]. The sulphate produced ($BaSO_4$) comes out as a heavy, powdery, white precipitate, which, *unlike any other baryta-salt precipitate*, is absolutely insoluble in water, and almost insoluble in even hot dilute acids.

30. Take a solution of (*a*) sulphate of soda; (*b*) phosphate of soda, and to each add chloride of barium. In (*a*) a precipitate of sulphate, in (*b*) one of phosphate of baryta is produced. Now add hydrochloric acid to both mixtures; the phosphate (*b*) dissolves; the sulphate remains.

(*c*) *Sulphuric Acid as a Reagent.*

31. Take solutions of the following salts : (*a*) chloride of strontium; (*b*) nitrate of lead; (*c*) mercurous nitrate; (*d*) chloride of calcium; (*e*) chloride of magnesium; and to each add dilute sulphuric acid. The effect is as follows :

<table>
<tr><td>Sol. of (BaO),SrO,PbO.</td><td>Hg_2O.</td><td>CaO,MgO-Salt.</td></tr>
<tr><td>The whole *</td><td>The bulk *</td><td rowspan="2">No precipitate. Add ½ vol. of alcohol; the Ca is precipitated; the Mg remains in solution.</td></tr>
<tr><td colspan="2">of the metal is precipitated as a sulphate, $MOSO_3$,† insoluble, or almost so, in the acid liberated.</td></tr>
</table>

Verify these statements as far as you are able. Take note of the fact, that what was stated for MgO-salt holds for the salts of *any* (ordinary) metallic base not BaO, SrO, PbO, Hg_2O; and you will understand how to use sulphuric acid as a generic precipitant for these bases, and even as a specific test for CaO.

---

* Supposing a sufficiency of reagent to have been added.

† 'M' here stands as a general symbol for Ba, Sr, Pb, Hg_2.

Hydrochloric Acid, HCl (*syn.: Muriatic Acid*).

(*a*) *Its Properties.*

32. Take a few decigrams of common salt, NaCl, and treat it in a test-tube with oil of vitriol: dense fumes of hydrochloric acid (HCl, or rather a mixture of HCl and H_2O) will come off. Observe the action of these fumes on your respiratory organs, on litmus; on ammonia-gas, NH_3, by letting them strike against a glass rod moistened with aqueous ammonia.

33. Examine a specimen of fuming muriatic acid (aqueous acid containing, say, 30 per cent. or more of HCl). Heat some of it in a test-tube to boiling, and observe the effect. Then dilute some of the acid with five times its volume of water; again heat to boiling, and examine the vapours with litmus-paper. You will find them to be neutral, shewing that they consist of pure steam. Remember that hydrochloric acid, although a gas, is not volatilised from sufficiently dilute aqueous solutions on boiling. In fact, considering it as a wet-way reagent, it is a non-gaseous, relatively little volatile acid. It accordingly readily decomposes carbonates and sulphides, with evolution of carbonic-acid gas and sulphuretted-hydrogen gas respectively. Verify this by trying the action of the aqueous acid on marble and on sulphide of iron. In either case the chloride ($CaCl_2$, $FeCl_2$) formed remains dissolved. In fact, all muriates (chlorides corresponding to basic oxides) are soluble in water, *with a few exceptions.*

(*b*) *Reactions of Chlorides.*

34. Take solutions of the nitrates of (*a*) silver oxide, Ag_2O; (*b*) mercurous oxide, Hg_2O; (*c*) lead oxide, PbO; (*d*) cupric oxide (any other salts of the same bases will do, if only soluble in water or dilute nitric acid), and examine the action on them of hydrochloric acid. The effects are as follows:

(*a*)	(*b*)	(*c*)	(*d*)
Ag_2O.	Hg_2O.	PbO.	CuO.*
The whole		Almost the whole	None

of the metal is precipitated.

Precipitated is a	AgCl curdy	Hg_2Cl_2 powdery	$PbCl_2$ crystalline

white precipitate.

Insoluble	Soluble

in *boiling* water.

(*c*) *Hydrochloric Acid as a Reagent.*

35. Hence, supposing a solution of metallic salts, for example, nitrates, gave a precipitate with hydrochloric acid, this precipitate could contain only the muriates of Ag_2O, Hg_2O, PbO; other bases, if present, would remain dissolved. Supposing such a solution *to have been precipitated* with HCl as far as possible, the precipitate filtered off, and the filtrate then were found to give a strong precipitate with sulphuric acid; what might that precipitate consist of? Another query: Supposing a solution of, say, nitrates gave no precipitate on addition of sulphuric acid, but gave one on addition of hydrochloric; what would this prove?

36. Of the three insoluble chlorides named in 34, the silver salt is in the highest degree insoluble in water and acids, hence nitrate of silver is a better precipitant for chlorides than salts of either Hg_2O or PbO are. But a precipitate produced in a salt solution by $AgNO_3$ must not be taken as indicating chlorides unless it proves insoluble on addition of nitric; and even then, all that is really proved is that the solution contains a salt or salts of *a certain class* of acids, of which, however, hydrochloric is by far the most commonly occurring. To illustrate this:

37. Take solutions of (*a*) chloride; (*b*) bromide; (*c*) iodide; (*d*) phosphate of, say, sodium or potassium, and add to each nitrate of silver. All the solutions will become turbid. Now add nitric acid to each: the phosphate dissolves, the chloride, bromide, and iodide remain undissolved.

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* Or any other base not *a*, *b*, or *c*. Observe that salts of HgO are not precipitated by HCl.

Nitric Acid, HNO_3.

(*a*) *Its properties as such.*

38. Procure a supply of 'fuming nitric acid of 1·5 sp. gr.' This preparation is generally dark-brown from dissolved N_2O_3; if colourless, you may accept it as a sufficient apology for real HNO_3. Observe its properties: its heaviness, its action on a feather or on your epidermis); its apparent non-action on cotton-wool; the fumes which it emits in air; its action on water.

Dilute some with its own volume of water; the mixture no longer emits fumes. Dilute further to, say, 10 times the original volume; the solution now, if the original acid was brown, no longer has any colour; (the N_2O_3 having been decomposed by the action of the water into nitric acid, $H_2ON_2O_5$, and nitric oxide, NO); when boiled, it emits neutral vapours (of steam).

39. Observe the action of dilute nitric acid on caustic potash, ammonia, carbonate of soda, marble, $CaCO_3$. Explain reactions by equations.

(*b*) *Its Oxidising Action.*

40. Study the action of dilute nitric acid (of 1·2 sp. gr.) on small specimens of copper, lead, silver, platinum, gold.

41. Dissolve a bit of iron in dilute sulphuric acid, to produce $FeSO_4$, add a few drops of nitric acid, and heat. The liquid soon assumes a black colour and then clears up with evolution of nitric oxide, NO, and formation of a solution of ferric sulphate, $Fe_2(SO_4)_3$. The reaction consists in this, that the H_2 of some of the free H_2SO_4 in the solution is oxidised away, and the SO_4 liberated combines with the $Fe_2(SO_4)_2$. (Give equation.) In a similar manner nitric acid acts on many other substances capable of taking up oxygen (or additional acid-radicle).

42. Mix fuming hydrochloric acid with nitric acid of 1·4 sp. gr., and heat. The hydrochloric acid is oxidised by the nitric with formation of NO (which escapes and forms red fumes), of a volatile chloride, NO_2Cl, and of free chlorine. For ordinary analytical purposes, it is sufficient

to observe that the HCl is dehydrogenised by the nitric acid with formation of chlorine. Again produce some of the mixture, and let it act upon gold-leaf; the gold dissolves as $AuCl_3$ (hence the name of '*aqua regia*').

(*c*) *Reactions of Nitrates.*

43. Take note of the fact that nitric acid forms no insoluble normal salts with any ordinary base; but observe also that many nitrates are insoluble in strong nitric acid. [Thus, for instance, when lead is treated with excess of nitric acid of 1·2 sp. gr., the nitrate, $Pb(NO_3)_2$, formed separates out as a crystalline powder; when nitrate of baryta solution is poured into nitric acid (of 1·2 sp. gr. or more) a precipitate of $Ba(NO_3)_2$ is produced, which disappears on addition of much water.] Hence we have no precipitant for nitric acid; yet nitrates can be easily recognised—by the following tests:

44. (*a*) Take a little of a dilute solution of, say, potassic nitrate; add a drop of indigo and some sulphuric acid; there is no change, but on heating, the blue colour is destroyed: by a process of oxidation; hence the test only reveals the presence of loose oxygen, which needs not necessarily be there in the form of HNO_3. More characteristic is the following test:

45. (*b*) Take a little of a solution of a nitrate, *add its own volume* of oil of vitriol, allow to cool, and then pour on the top of the mixture some concentrated solution of *ferrous sulphate.* The ferrous-salt layer soon assumes a characteristic brown colour, owing to NO liberated from the nitric acid. This test proves the presence, at the same time, of oxidised nitrogen and loose oxygen, and hence goes further than (*a*); in fact, it proves the presence of nitrate or of nitrite.

Caustic Potash and similar Basic Hydrates.

46. Procure specimens of solid caustic potash; of solid caustic soda; of baryta, BaO; lime, CaO (quicklime). Observe their general properties; their behaviour (*a*) when exposed to ordinary air, (*b*) when treated with water.

47. Caustic potash and soda readily dissolve with evolution of heat; caustic lime and baryta[*] act violently on water with formation of hydrates, $CaOH_2O$, $BaOH_2O$, which, if excess of water be avoided, are obtained in the solid form. Solutions of caustic potash or soda ('caustic alkalies'), having the power of dissolving fats and other components of animal tissues, render the fingers slippery; even when very dilute, they colour red litmus-paper blue, and (yellow) turmeric-paper brown; they readily saturate all acids according to the general formula $XH(acid) + RHO = XR + HHO$.

48. Treat hydrate of lime with cold water, and filter. The filtrate contains about $\frac{1}{700}$th part of CaO in solution, as $Ca(OH)_2$, which small quantity is quite sufficient to give it the power of acting strongly on turmeric and red litmus paper. Blow through the lime-water by means of a glass tube; the carbonic acid, CO_2, of the expired air combines with the lime into carbonate, which separates out as a white precipitate. On continued blowing, the precipitate re-dissolves as an unstable bicarbonate, which, however, is readily decomposed on boiling.

49. Treat a few decigrams of hydrate of baryta with water at a boiling heat. The bulk of the substance readily dissolves, but there is always a white residue left. This residue, however, is easily proved to consist of carbonate, which practically is always present as an impurity. Filter off the residue. The filtrate, if not too dilute, deposits, on cooling, crystals of $Ba(OH)_2 8H_2O$, which are soluble in about twenty-five parts of cold water. The solution behaves to CO_2 like lime-water; and both to acids generally like caustic potash or soda.

50. To shew the action of carbonic acid on potash (or soda), take a little of a pure solution of, say, soda, and add excess of dilute sulphuric acid. No *gas* should be evolved. Then take another portion, blow CO_2 (expired air) through it for some time, and repeat the test. Bells of CO_2 will be evolved.

51. Heat a fragment of solid caustic potash in a silver

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[*] The student may operate with lime, and take the baryta for granted.

dish. It first fuses, and the fused mass next boils up through the escape from it of the extra water which it always contains, and at last pure KHO is left, which, at higher temperatures, goes off slowly as a whole, but never loses any of its own water. Take note of the fact that caustic soda, NaHO, and baryta, $Ba(OH)_2 = Ba_{\frac{1}{2}}OH$, behave similarly, while the lime compound, at a red-heat, readily breaks up into $CaO + H_2O$. These three hydrates (of K, Na, Ba) and that of Sr are the most powerful of fixed bases, and much used as such in analysis; caustic potash or soda being preferably employed.

Illustrations.

52. Take solutions of the nitrates or other soluble salts of (*a*) MgO; (*b*) Ag_2O; (*c*) HgO; (*d*) PbO; (*e*) ZnO; and add to each caustic soda as long as the precipitate formed increases, or until the mixture is decidedly alkaline to turmeric. The bases are all precipitated; *a*, *d*, and *e* as hydrates; *b* and *c* as oxides. Solutions of the salts of most heavy metallic bases behave similarly.* But in some cases the precipitated bases, when treated with excess of caustic soda (or KHO), combine with the alkali into soluble salts, in which they (that is, the insoluble bases) play the part of acids. To illustrate this by examples, add excess of caustic soda to mixtures *d* and *e*: the precipitates disappear.

53. To a solution of *sal-ammoniac* add some caustic soda, and heat. Ammonia-gas, NH_3, is evolved, which is readily recognised by its characteristic pungent smell, by its alkaline reaction on turmeric or red litmus paper, and by the clouds (of NH_4Cl) which it forms when brought into contact with a glass rod moistened with aqueous hydrochloric acid—that is, with HCl-gas.

Ammonia is largely soluble in water, forming a solution which, although it quickly loses its NH_3 on boiling, behaves to acids and metallic salts like one of KHO, and consequently may be assumed to contain a (highly unstable) hydrate of 'ammonium,' $(NH_4)OH$, analogous to KOH. But observe that, whilst in most of these reactions (as applied in analysis) KHO and NaHO may unhesitatingly be substituted for each other, aqueous ammonia [the imaginary $(NH_4)OH$] not unfrequently exhibits peculiar properties. To illustrate this:

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* Sometimes a basic salt is produced instead of pure hydrate or oxide.

54. Mix solutions of sulphate of copper with (*a*) excess of caustic soda; (*b*) excess of ammonia, and observe the effects. In the case (*a*) heat the mixture to boiling, and note the change. Report (in your book) on these and the previous observations, using equations where possible.

Carbonic Acid, H_2CO_3, *and Carbonates.*

55. Place a piece of marble in a test-tube, and add dilute hydrochloric or nitric acid. The marble dissolves with evolution of (gaseous) 'carbonic acid,' $CO_2 = CO_3H_2 - H_2O$, of which a considerable quantity, on account of its heaviness, remains in the tube. Pour out the CO_2 (not the liquid contents) into another test-tube previously charged with some clear *lime-water*, and shake up. An abundant precipitate of $CaCO_3$ is produced. This is a perfectly general and characteristic test for carbonates.

56. Procure characteristic specimens of carbonate of soda crystals, $Na_2CO_3 + 10H_2O$; pure soda-ash, Na_2CO_3; bicarbonate of soda, $NaHCO_3$; carbonate of potash (pure pearl-ash), K_2CO_3; bicarbonate of potash, $KHCO_3$; sesquicarbonate of ammonia, $2(NH_4)_2O,3CO_2$ [this, and the bicarbonate, $(NH_4)HCO_3$, are the only known solid carbonates of ammonium]; and study them in regard to (1) Their general appearance, smell, taste; (2) Their behaviour when heated on platinum foil; (3) Their behaviour to water (*a*) in the cold, (*b*) in the heat and on boiling; (4) The action, of the solutions made in the cold, on turmeric-paper.

57. Heat some bicarbonate of soda in a dry test-tube: the salt breaks up into Na_2CO_3 and CO_2. Identify the latter.

58. Almost all metallic carbonates (except those just treated of) are insoluble, or little soluble in water. Hence

solutions of the salts of almost all metallic bases not alkalies, when mixed with solutions of carbonate of potash or soda, give precipitates of the respective carbonates (which, however, are not necessarily normal salts). The action of carbonate of ammonia, however, is often peculiar. Yet it is preferably employed as a precipitant for metals in analysis.

Carbonate of Ammonia as a Reagent.

59. Take a solution of sulphate of copper, and add, drop by drop, a solution of carbonate of ammonia* as long as there is a visible change. The first instalments of reagent produce a precipitate which, however, dissolves in excess into a dark-blue liquid. A few other heavy-metallic salts behave similarly.

60. Repeat the experiment with a solution of (say, acetate of) lead. A *permanent* (white) precipitate is formed. *Most* heavy-metallic salts behave in *this* manner.

61. Take solutions of (say, chlorides of) barium, strontium, calcium, magnesium (the magnesium solution should be pretty concentrated), and add to each carbonate of ammonia in excess—that is, enough to produce a strongly alkaline liquid. The Ba, Sr, and Ca salts give immediate precipitates of the respective normal carbonates, MCO_3, which, especially when the mixtures were heated, contain practically the whole of the metal. The magnesium solution may remain clear at first, but if the normal carbonate $(NH_4)_2CO_3$ was used, and a sufficient excess of it added, the mixture, especially when stirred up, soon becomes turbid, and gradually deposits almost the whole of its magnesium in the form of a crystalline double salt, $MgCO_3(NH_4)_2CO_3 + 4H_2O$.

62. Take a dilute solution of *magnesia salt*, add some sal-ammoniac, NH_4Cl, solution, and then a moderate quantity of carbonate of ammonia : the solution remains clear, even on heating. The presence of sal-ammoniac does not interfere materially with the action of carbonate of ammonia on

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* A solution of sesquicarbonate mixed with the proper proportion of NH_3 to produce $(NH_4)_2CO_3$. In most cases sesquicarbonate of ammonia may be substituted for it without inconvenience.

Ba, Sr, and Ca salts. Hence, in the presence of NH_4Cl, these three metals can be precipitated by carbonate of ammonia in presence of magnesium, and thus be separated from, or detected (as a group) in the presence of, the latter: supposing, of course, the solution is known not to contain anything except (possibly) salts of Ba, Sr, Ca, Mg, K, Na, NH_4.

Orthophosphoric Acid, H_3PO_4.

63. *Preliminary Note.*—By burning phosphorus in excess of oxygen or air, we obtain the anhydride, P_2O_5, as a white, snow-like powder, which is slowly volatile at a red-heat. When treated with water, it combines with it with great evolution of heat into 'metaphosphoric acid,' $H_2O . P_2O_5$, which at first appears in the form of a gelatinous precipitate, but, after some time, dissolves in the excess of water *as such*, forming a strongly acid solution. When this solution is boiled, it passes into one of orthophosphoric acid. In performing the following experiments, the student had better start with a ready-made solution of the latter.

64. Place some of the solution on a concave platinum crucible lid, boil it down, and next satisfy yourself that the vapours are neutral to litmus-paper, and consequently consist of pure water; continue the evaporation as long as any visible steam goes off, and then go on heating until the residue has for several minutes been at a dull red-heat. The effect is that the orthophosphoric acid which is left when all the free H_2O is gone, passes quickly through pyrophosphoric ($P_2O_52H_2O$) into metaphosphoric acid, which is perfectly stable at a dull red-heat.

Dissolve your meta-acid in water, and add nitrate of silver; a white precipitate of metaphosphate of silver, $AgPO_3$ or $Ag_2OP_2O_5$, is produced.

Orthophosphates.

65. Take separate portions of orthophosphoric acid, and slightly supersaturate them with (*a*) ammonia; (*b*) carbonate of soda with application of heat; (*c*) baryta-water; (*d*) lime-

water. The effects are as follows: *a* and *b* are converted into solutions of di-metallic phosphates, $PO_4(NH_4)_2H$ and PO_4Na_2H respectively, which, though hydric salts, have an alkaline reaction. The acid in *c* and *d* is converted into an insoluble tri-metallic phosphate, which assumes the form of a precipitate (PO_4ba_3 and PO_4ca_3 respectively, where ba = ½ Ba, ca = ½ Ca).

Tests for Orthophosphates.

66. Take solution *b* (of Na_2HPO_4), dilute it, and add to it a solution of sulphate or chloride of magnesium. Perhaps there will be a precipitate [of $(PO_4)_2Mg_3$] produced, but in any case the precipitation is *slow*, and it is never complete; that is, neither the P_2O_5 nor the MgO will, under any circumstances, be completely precipitated. If necessary, repeat the experiment with solutions so dilute that no immediate precipitate at least is produced.

67. Then add some *sal-ammoniac*, and some free ammonia. The mixture will become turbid at once or (if very dilute) on standing, and, as the case may be, either the MgO or the P_2O_5 will at last be completely precipitated as $PO_4Mg(NH_4) + 6H_2O$: a crystalline precipitate, insoluble in dilute aqueous ammonia, even in the presence of ammonia-salts, though appreciably soluble in water and in neutral ammonia-salt solutions. It also is readily soluble in any of the ordinary aqueous acids, even in acetic. The sal-ammoniac is added to prevent the precipitation of $Mg(OH)_2$.

68. Add sulphate of magnesia to solution *b* [of $PO_4(NH_4)_2H$], and then some more ammonia. The same precipitate of PO_4MgNH_4 makes its appearance, but it is less likely to be contaminated with foreign MgO salts.

69. This reaction is highly* characteristic of orthophosphoric acid. The ordinary mode of executing it is as follows: Prepare *magnesia mixture* by adding to a solution of chloride of magnesium a sufficiency of sal-ammoniac, to

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* Absolutely, we should say, if it were not for the fact that arsenic acid, AsO_4H_3, acts in a perfectly similar manner.

prevent its being precipitated by ammonia, and then the proper proportion of free ammonia. To test a substance for orthophosphate, dissolve it in water if possible, or in hydrochloric (or nitric acid) if necessary, and then add *excess of ammonia*. Filter off any precipitate that may have been produced, add to the filtrate magnesia mixture, stir up and allow to stand. The P_2O_5 of the *solution* will gradually come down in the form of the characteristic magnesia-ammonia salt. But obviously, in cases where the ammonia produced a precipitate, the P_2O_5, instead of passing into the filtrate, *may* go partially or even wholly into the precipitate.

70. Dissolve some phosphate of zinc, or copper, or nickel[*] in hydrochloric acid, and add excess of ammonia; a clear (and in the case of zinc also colourless) solution is produced which, of course, necessarily contains all the P_2O_5. Add magnesia mixture: the P_2O_5 comes down in the well-known form.

71. Repeat the experiment with some tri-calcic phosphate $Ca_3(PO_4)_2$ instead of the zinc, &c. salt. In this case the ammonia produces a precipitate which is simply *identical* with the original substance, and consequently the filtrate, we should say, contains no phosphoric acid at all. (In practice a trace of the phosphate of lime remains dissolved, and the filtrate does give a very slight precipitate with the reagent.)

72. To detect the phosphoric acid in the ammonia precipitate produced (in 71), dissolve that precipitate in nitric acid, add the solution to a large excess of a *nitric* solution of molybdate of ammonia, and heat gently; the whole of the P_2O_5 is precipitated in the shape of yellow powdery phospho-molybdate of ammonia $[PO_4(NH_4)_3 . 10MoO_3]$. This is a perfectly general test for all phosphates soluble in nitric acid.[†]

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[*] If the phosphates are not at hand, take the chlorides, add some phosphate of soda, dissolve the precipitate in HCl, and add excess of ammonia.

[†] Liable to the qualification stated in foot-note to sect. 69, page 25.

Orthophosphate as a Reagent.

73. Just as magnesia-mixture is a very delicate precipitant for phosphoric acid; so, under similar conditions, phosphate of ammonia or soda (when used along with ammonia) is an equally delicate precipitant for magnesia. But as most orthophosphates (not alkali-salts) are insoluble, or almost so, in water and salt solutions, the reaction, *as a test for* MgO, is restricted to the case where it is proved that the solution contains nothing but, possibly, Mg, K, Na, NH_4 salts.

In your report explain all the reactions executed by equations. State what you think will go on when a solution of the salt PO_4ca_2H ($ca = \frac{1}{2}Ca$) in hydrochloric acid is mixed with excess of ammonia.

Sulphuretted Hydrogen, H_2S, *and its Salts.*

74. Place a granule of sulphide of iron, FeS,* in a test-tube and add some hydrochloric acid. The sulphide dissolves as $FeCl_2$, with evolution of sulphuretted-hydrogen gas, which is easily recognised, even when largely diluted with air or other inert gases, by its smell, and by its colouring acetate of lead or sulphate of copper paper dark brown or black. This test applies to all metallic sulphides decomposable by HCl.

75. *Preparation of Sulphuretted Hydrogen.*—Place in a gas-evolution bottle from 30 to 50 grammes of fused *sulphide of iron*, FeS, and add, through the funnel tube, commercial hydrochloric acid of about 10 per cent. When the gas-evolution slackens, add some more acid, and so go on until a sufficiency of gas is produced. Pass the sulphuretted hydrogen first through a tube loosely filled with cotton-wool in order to free the gas from small particles of liquid mechanically carried over, and then through air-free † distilled water contained in a phial as long as some of it is

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* Iron pyrites, FeS_2, will not do.

† Boil the water in a narrow-necked flask for five minutes, cork up well, and allow to cool.

absorbed. To see if the liquid is perfectly saturated with gas, close the mouth of the bottle, violently shake it, then turn the bottle upside down, and carefully slacken the stopper. As long as the water is not perfectly saturated, air bubbles are sucked in; if the point of saturation has been reached, part of the liquid is forced out. When the water is completely saturated, close the phial with a cork, and preserve it for use (best with mouth turned downwards).

76. *Preparation of Sulphide of Ammonium.*—Pass *sulphuretted hydrogen* through a measured volume, say 50 c.c., of a solution of *ammonia* (of about 10 per cent.) until it is completely saturated, then add another volume (50 c.c.) of ammonia solution, mix the two liquids, and keep the solution as one of *sulphide of ammonium.* The processes going on are represented by the following equations: (1) $NH_3 + H_2S = NH_4 . HS$. (2) $NH_4 . HS + NH_4 . HO = (NH_4)_2S + H_2O$. Or, condensing (1) and (2) into one: $H_2S + 2NH_3 = (NH_4)_2S$. Recently prepared aqueous sulphide of ammonium is a colourless liquid, possessing a strong alkaline reaction; when mixed with excess of any free acid it yields sulphuretted hydrogen and a clear solution of ammonia-salt; example: $(NH_4)_2S + H_2SO_4 = (NH_4)_2SO_4 + H_2S$. A solution of sulphide of ammonium readily absorbs oxygen from the atmosphere, and thereby assumes a yellow colour, a part of the compound $(NH_4)_2S$ being converted into *disulphide* $(NH_4)_2S_2$. (1) $(NH_4)_2S + O = (NH_4)_2O + S$. (2) $S + (NH_4)_2S = (NH_4)_2S_2$. The *yellow* solution, when mixed with acid, gives (beside NH_4-salt and H_2S-gas) a white milky precipitate of sulphur. $(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S$. A slight admixture of disulphide does not interfere with most of the purposes for which the reagent is used in analysis.

H_2S-*Salts of other bases than* $(NH_4)_2O$.

77. When, in the experiment just described, we substitute potash, soda, baryta, strontia, or lime solution for ammonia, the effect is quite analogous to the one obtained with that base. An excess of H_2S produces solutions of sulphhydrates, RHS or $R''H_2S_2$; and the solutions of RHS, that

is, of KHS or $NaHS$, by addition of RHO are converted into solutions of R_2S—for example :

$$RHS + RHO = R_2S + H_2O ;$$

but with the bodies $R''H_2S_2$, for example, with $Ba''H_2S_2$, this change *cannot* be effected, because the sulphides $R''S$, if they *were* produced, would be decomposed by the action of water into $R''(HS)_2$ and $R''(HO)_2$. To pass now to the rest of the metallic oxides which we have space in this book to notice, we have to mention :

78. (1) That the hydrates of MgO, Al_2O_3, Cr_2O_3, are *not* changed by the action of H_2S, which includes that solutions of the salts of these oxides are not acted upon by H_2S—nor by sulphide of ammonium, one would be inclined to add ; but this surmise is not quite borne out by experience. It is with magnesia ; but solutions of Cr_2O_3 and Al_2O_3, when mixed with sulphide of ammonium, give precipitates, containing the metals—not as sulphides, it is true, but as hydrates ; the reagent acting as if it were decomposed by the water present into ammonia and sulphuretted hydrogen. On this occasion we may refer

79. (2) To a group of three oxides—namely, Fe_2O_3, and the two acid oxides CrO_3 and Mn_2O_7, which, although not convertible into sulphides under the circumstances, are, by the action of *sulphuretted hydrogen* on their solutions in excess of mineral acid, reduced, the

	Fe_2O_3	CrO_3	Mn_2O_7
to salts of	FeO	Cr_2O_3	MnO

with precipitation of *sulphur*.

80. (3) The metallic oxides which still remain to be considered all agree in this, that, supposing them to be given as solutions in aqueous acids or alkalies, they are, by means of H_2S, or at least by the conjoint action of H_2S and NH_3, that is by $(NH_4)_2S$, convertible into sulphides, which are all insoluble in water and ordinary salt solutions, and, when produced, assume the form of *precipitates*. But according to the circumstances under which these sulphide-precipitates are produced, they arrange themselves into three groups, as shewn by the following :

TABLE I.—SHEWING THE ACTION OF H_2S AND OF $(NH_4)_2S$ ON SOLUTIONS OF

<table>
<tr><td>81.</td><td>I.
As_2O_3;
(As_2O_5);
Sb_2O_3; Sb_2O_5;
SnO_2; (SnO).*</td><td>II.
Bi_2O_3; CuO;
CdO; HgO;
Hg_2O; PbO;
Ag_2O; (SnO).</td><td>III.
FeO; MnO;
ZnO;
NiO; CoO;
[Cr_2O_3; Al_2O_3].</td></tr>
<tr><td><i>Sulphuretted hydrogen in the presence of free acid.</i></td><td colspan="2">The metals are completely precipitated as sulphides</td><td>The metals remain dissolved.</td></tr>
<tr><td></td><td>soluble in</td><td>insoluble in</td><td></td></tr>
<tr><td></td><td colspan="2"><i>sulphide of ammonium.</i>†</td><td></td></tr>
<tr><td><i>Sulphide of Ammonium.</i></td><td>In the presence of enough of free alkali; <i>no precipitate.</i></td><td colspan="2">In the absence of free acid, the metals are completely precipitated as</td></tr>
<tr><td></td><td></td><td><i>sulphides.</i></td><td><i>sulphides</i>
[Cr and Al as hydrates].</td></tr>
<tr><td></td><td></td><td colspan="2">Insoluble in excess of reagent, as also in ammonia and in sal-ammoniac.</td></tr>
</table>

82. *Note regarding Group III.*—The precipitates are readily dissolved by even cold dilute hydrochloric acid [the Cr_2O_3 and Al_2O_3 *without* evolution of H_2S]; except NiS and CoS, which, when once produced, are hardly attacked in the cold by 5 per cent. HCl.

Discrimination of Groups of Metallic Oxides.

83. We see, then, that (in reference to solutions producible by dissolving metallic oxides in mineral acids) we

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* Also PtO_2, Au_2O_3; MoO_3, WoO_3; but we must ignore these, like some other, rare oxides.

† SnO appears both under I. and II., because, while insoluble in real $(NH_4)_2S$, it is dissolved by the *yellow* reagent $(NH_4)_2S.S$, and as $SnS_2.2(NH_4)_2S$. (As_2O_5) is inclosed in brackets, because its action on H_2S is exceptional. See sect. 130.

can, by means of H_2S and $(NH_4)_2S$ as precipitants, discriminate between four groups of metallic oxides, namely, Groups I., II., III. of Table I., and—a Group IV. (comprising BaO, SrO, CaO, MgO, and the alkalies), the metals of which are *not* precipitated by H_2S or $(NH_4)_2S$ under *any* circumstances.

84. The student will also observe that, assuming any metal of Group III. to have been precipitated from its solution by $(NH_4)_2S$, the application to the (*washed*) precipitate of HCl would enable him to discriminate between the sub-groups A = Co and Ni; B = Cr and Al; C = Fe, Mn, Zn.

85. But *Hydrochloric Acid*, as shewn in sect. 34, when applied directly to a solution of metallic salts, is a specific precipitant for the group Ag_2O, Hg_2O, PbO; while

86. *Sulphuric Acid* precipitates only, and thus characterises as a group, the oxides PbO; Hg_2O; BaO, SrO. We are thus enabled to split up our Group II. into three sub-groups—namely:

(*A*) Ag_2O..................Precipitated by HCl; not by H_2SO_4.
(*B*) Hg_2O and PbO... " " HCl and by H_2SO_4.
(*C*) The rest.............Not precipitated by either.

We will now leave Groups I., II., and III. on one side, and tabulate the reactions with solutions of Group IV. of sulphuric acid, carbonate of ammonia, and phosphate of ammonia, as set forth in sects. 31, 61, 62, 66 to 69, and 73.

87. TABLE II.—REACTIONS OF GROUP IV.

(*a*) *Action of excess of Sulphuric Acid on Solutions of* (salts of)

BaO.	SrO.	CaO.	MgO.	Alkalies.
Metals precipitated as sulphates.		No precipitate in dilute solutions.	No precipitate.	
On addition of ½ vol. of alcohol.				
Metals precipitated			No precipitate.	
more completely.		gradually, but at last completely.		

(*b*) *Action of Carbonate of Ammonia in the presence of sal-ammoniac.*

BaO.	SrO.	CaO.	MgO.	Alkalies.
Metals precipitated as carbonates $R''CO_3$; more completely on heating.			Metals remain dissolved.	

(*c*) *Action of Phosphate of Ammonia in the presence of sal-ammoniac and free ammonia.*

Metals more or less completely precipitated as phosphates.	Metal is gradually, but at last completely precipitated as PO_4MgNH_4.	No precipitate.

88. The reactions embodied in these tabular statements (sects. 81 to 87) constitute, so to say, the ABC of metal-analysis, and like the ABC of a language, must be committed to memory. For this purpose the student should draw up a large table, which, in so many vertical columns, enumerates the several groups of oxides which we have learned to distinguish from one another—thus:

Ag_2O, Hg_2O, PbO.	HgO, CuO, Bi_2O_3, CdO.	As_2O_3, Sb_2O_3, SnO, SnO_2.	As_2O_5.
'Silver group.'	'Copper group.'	'Arsenic group.'	

CrO_3, Mn_2O_7, Fe_2O_3.	Al_2O_3, Cr_2O_3.	FeO, MnO, ZnO.	NiO, CoO.
'Iron group.'			

BaO, SrO.	CaO.	MgO.	K_2O, Na_2O, $(NH_4)_2O$.
'Barium group.'			'Alkalies.'

And then in so many horizontal columns put down, in as few words as possible, the reactions on solutions of the several groups of oxides, of the several generic reagents, HCl, H_2SO_4, H_2S, $(NH_4)_2S$, $(NH_4)_2CO_3$, $PO_4(NH_4)_3$.*

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* Remember the names given between inverted commas; they will be used in the following chapters.

EXERCISES ILLUSTRATIVE OF THESE GENERIC REACTIONS.

Sulphides of Groups I. and II.

89. Dissolve a few centigrams of *white arsenic* (As_2O_3) in aqueous *hydrochloric acid*, and add to the solution of $AsCl_3$ thus obtained *sulphuretted-hydrogen water*, until the liquid, after thorough shaking, smells strongly of the gas. Insoluble sulphide of arsenic (As_2S_3) is precipitated, hydrochloric acid goes into solution : $2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$. Collect the yellow precipitate on a filter, wash it with water until the wash-water no longer contains hydrochloric acid (reddens litmus); then pour on the precipitate some sulphide of ammonium; the precipitate dissolves, being converted into a soluble double sulphide, $As_2S_3x(NH_4)_2S$. If we acidify this solution with hydrochloric acid, the sulphide of ammonium is decomposed (*vide supra*), and the sulphide of arsenic reprecipitated.

90. Mix a solution of *nitrate of bismuth* with an excess of *sulphuretted-hydrogen water;* the bismuth is completely converted into a brown precipitate of *sulphide of bismuth*, while nitric acid passes into solution. Wash the precipitate with water, and treat it with *sulphide of ammonium;* it does not at all dissolve. The filtered liquid, when acidified with hydrochloric acid, yields sulphuretted hydrogen, and a solution of chloride of ammonium, mixed perhaps with more or less of a milky precipitate of sulphur, but no sulphide of bismuth is separated out.

Sulphides of Group III.

91. Dissolve a few centigrams of *ferrous sulphate* in water acidified slightly with sulphuric acid, and add some *sulphuretted-hydrogen water:* there will be no visible change. Now add an excess of *ammonia:* a black precipitate is formed, which, if a sufficiency of sulphuretted hydrogen has been used, contains the *whole* of the iron as sulphide, FeS. The same result is obtained by adding to the iron solution—instead of sulphuretted hydrogen and

ammonia—a ready-made solution of ***sulphide of ammonium***, the reaction corresponding in both cases to the equation: $FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4$. Collect the precipitate of sulphide of iron on a filter, and add to it some dilute sulphuric (or hydrochloric) acid; it dissolves with evolution of sulphuretted hydrogen, a solution of ferrous sulphate (or chloride) being formed. Preserve liquor for exercise, sect. 93.

92. Repeat the last exercise with chloride of *cobalt*, instead of the ferrous salt. The result will be similar, except that the precipitated black sulphide, when treated on the filter with a mixture of the ordinary (20 per cent.) hydrochloric acid with two to three times its volume of water *in the cold*, will remain unchanged—substantially at least. Neutralise the acid filtrate with ammonia; only a very slight turbidity (of re-generated CoS) will be produced.

Pseudo-sulphide Precipitates.

93. Take some solution of ferrous chloride containing free HCl (for example, the liquor produced from FeS and acid in Exercise 91), add a few granules of chlorate of potash, and boil: the ferrous salt is 'oxidised' (as the phrase goes) into ferric salt; that is, the muriate of the oxide FeO is converted into that of the oxide Fe_2O_3—that is, into Fe_2Cl_6, which imparts to the liquid a yellow colour, which is very intense, as long as the liquid is hot. Filter off the precipitated sulphur, which will be present if you used the mixture of FeS with HCl, and add excess of *sulphuretted-hydrogen water*. The mixture, after having for a moment exhibited a transitory blue colour, becomes turbid and white from precipitated sulphur. The solution now is one of $FeCl_2$, which, after saturation of the free acid with ammonia, behaves to sulphide of ammonium as shewn in exercise, sect. 91.

Note.—From ferric salts, sulphide of ammonium precipitates a *mixture* of $2FeS + S$, a kind of pseudo Fe_2S_3.

94. Take a solution of *bichromate of potash*, add to it some hydrochloric acid (to produce a mixed solution of CrO_3 and

free HCl), and pass sulphuretted hydrogen through the liquid. The liquid becomes turbid from precipitated sulphur, and the originally intense garnet-red colour of the liquid undergoes a decided change. As soon as the liquid is *saturated* with H_2S (see sect. 89), filter the mixture, one-half (*a*) as it is, the other (*b*) after boiling. The filtrate (*a*) has an intense violet, that of (*b*) an equally intense green colour; both contain the original chromium as chromic chloride, Cr_2Cl_6 (muriate of Cr_2O_3).

95. To the solution of Cr_2O_3 produced, add ammonia, until the precipitate, which appears locally from the first, is very slow in disappearing when the mixture is shaken (shewing that the free acid is saturated); then add excess of sulphide of ammonium (that is, more than enough to precipitate the whole of the chromium), and filter. Wash the precipitate with water until the last washings are free of H_2S or $(NH_4)_2S$; then dissolve it in cold dilute hydrochloric acid, and add to the solution some cupric salt. There will be *no* turbidity of CuS produced, which proves that the precipitate cannot have been a sulphide such as Cr_2S_3, but must have been a hydrated oxide, $Cr_2O_3 + xH_2O$.

Bases not convertible into Sulphide-Precipitates.

96. Take, successively, solutions of $BaCl_2$, $MgCl_2$, KCl, and satisfy yourself that they behave to the several generic reagents as stated in our tables.

Separations.

(*a*) *Silver Group from other Groups.*

97. The alloy which 'silver' coins are made of consists of silver and copper, associated generally with a trace of gold. To analyse a sample (you may work on, say, a threepenny piece), dissolve it in nitric acid of 1·2 sp. gr. in the heat. The gold remains as a black powder, which is filtered off, and can be obtained by itself by incinerating the filter in a porcelain crucible. The filtrate contains the copper and silver as nitrates. To separate out the silver, add to the solution hydrochloric acid, drop by drop, shaking up after each addition until the last drop does not produce an

additional turbidity. Shake up violently, until the mixture has lost its milky appearance, then allow the precipitate (AgCl) to settle, and decant the (blue) copper solution through a filter. Wash the precipitate by decantation with water until the last washings are free from copper, and add the more concentrated portions of the wash-water to the original decantate. From the latter the copper must now be precipitated by sulphuretted hydrogen, but this is not easily effected by the direct application of this reagent, because a considerable portion of it would be oxidised by the nitric acid present. Hence we first of all displace, so to say, the nitric by hydrochloric acid, which is done by boiling down the liquor in a flask to a small bulk, adding, say, twice its volume of strong hydrochloric acid, and boiling down again as far as conveniently possible.* The residue now is sufficiently free of nitric acid to be treated with sulphuretted hydrogen.

(*b*) *Groups I., II., and III. from one another.*

98. Prepare a solution containing the chlorides of *arsenic*, *bismuth*, *iron* (ferrous), and then separate from one another these metals with the help of the reactions before given for the individual metals—that is:

(1) Dilute the liquid and pass in *sulphuretted-hydrogen gas*, so as to completely precipitate the arsenic and bismuth as sulphides; wash the precipitate with water until the last washings no longer contain iron (that is, until they no longer give a coloration with sulphide of ammonium, or after evaporation in a small platinum dish, leave no residue non-volatile at a red-heat). Mix the sulphides on the filter with *sulphide of ammonium*, taking care at first not to tear the paper, then pierce the bottom of the filter with a pointed glass rod, let the mixture run into a flask, and heat it gently for about five minutes, so as to completely dissolve the sulphide of arsenic. Collect the sulphide of bismuth on a new filter, wash it with luke-

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* This second evaporation (in other cases) when arsenic, antimony *may* be present, had better be done in a retort connected with a condenser, so as not to lose any volatile chlorides.

warm water (always adding at the same time some sulphide of ammonium) until at last the wash-water no longer contains arsenic—that is, behaves to hydrochloric acid like a very dilute solution of sulphide of ammonium. From the filtrate, mixed with the more concentrated portions of the washings, precipitate the *arsenic* (as sulphide) by acidification with hydrochloric acid, collect the precipitate on a filter, and free it from the chloride of ammonium adhering to it by repeated washing with water.

99. (2) To the *filtrate from the arsenic and bismuth* precipitate add, first, enough of ammonia to completely saturate the free hydrochloric acid it contains, and then a sufficient quantity of *sulphide of ammonium* to precipitate the whole of the *iron*. In order to see whether the mixture contains a *sufficiency* of precipitant, lift out a drop of it by means of a glass rod, and place it on a *double* bit of filter-paper. If free sulphide of ammonium is present, the lower bit of paper becomes *black* when moistened with acetate of *lead*. Complete the precipitation, and collect the precipitate on a filter. [The filtration is considerably facilitated by adding to the mixture (if necessary) some more chloride of ammonium, gently heating and then violently shaking it.] Wash the sulphide of iron with warm water (mixed with a little sulphide of ammonium to protect the precipitate against the oxidising action of the atmosphere) until the last runnings, when evaporated at a gentle heat on a strip of glass, leave no residue except perhaps a trace of free sulphur from the (yellow) sulphide of ammonium added to the wash-water.

100. Pour some dilute hydrochloric acid on the sulphide of iron in the filter; it should dissolve completely; if a black residue is left, this proves that the bismuth had not been completely precipitated by sulphuretted hydrogen. *The analysis in this case must be repeated.*

Queries: Supposing the solution, besides the metals which you put in, had contained barium; where would it be, and how could it be separated out? Supposing, secondly, it had contained cobalt, where would it have gone, and how could it be separated out as pure CoS?

101. Take some of the same mixed solution as served for the last exercise, and in order now to merely prove that the solution contains a metal of the arsenic group, add firstly ammonia, drop by drop, until there is a small permanent precipitate produced; and after having thus saturated the free acid (to some extent), add excess of sulphide of ammonium, heat gently for some minutes, and filter. Acidify the filtrate with hydrochloric acid: the arsenic will be precipitated as As_2S_3 mixed with more or less of free sulphur. The mere appearance of the precipitate, in this and in any analogous case, proves that it must contain a metallic sulphide, but it does not always necessarily follow that that sulphide is an arsenic-group one, as shewn by the following exercise:

Peculiarities of certain Sulphides.

102. To a solution of *cupric sulphate* add some drops of ammonia, and, without minding the precipitate produced, excess of *yellow* sulphide of ammonium. Heat gently, filter, and acidify the filtrate. The precipitated sulphur is obviously metalliferous, but the metal in it consists merely of a trace of copper which has passed into solution. Remember that CuS is slightly soluble in sulphide of ammonium, and consequently apt to be mistaken for an arsenic-group sulphide. A few other difficulties which may present themselves in the examination of a solution for oxides of Groups I., II., and III. are illustrated in the following exercises:

103. Take a solution of *stannous chloride*, add to a small portion excess of sulphuretted-hydrogen water, and observe the effect. Then add to another portion, first, enough of ammonia to saturate the free acid, and then of *recently made* (colourless) sulphide of ammonium, until the mixture when tested, as shewn in sect. 99, is found to contain an excess of the reagent. Then add more of the latter, heat gently, and observe the effect; the brown precipitate remains undissolved. Now add to the mixture a pinch of flowers of sulphur and heat again; the precipitate will now vanish

with formation of a yellow solution, which when acidified gives a yellow precipitate of *stannic* sulphide, SnS_2.

104. To a solution of *sulphate of cadmium* (which should contain no excess of acid) add sulphuretted hydrogen (best in the form of gas); the metal is precipitated as a yellow sulphide, CdS. Now add to the mixture, gradually, more and more of fuming hydrochloric acid; it will not take very much of the acid to dissolve the whole of the yellow sulphide. When the last trace of the latter is gone, add water; the sulphide, when the liquid is sufficiently diluted, will reappear, but it may take a very large proportion of water to effect as complete as possible a precipitation.

105. To an *un-acidified* solution of chloride or sulphate of *zinc*, add sulphuretted hydrogen water; a *considerable* portion of the metal will come down as a white sulphide, to dissolve which takes a pretty considerable quantity of hydrochloric acid, although a somewhat smaller proportion of the acid, when added to the original liquid before the sulphuretted hydrogen, suffices to *prevent* the formation of the sulphide. Contrast this experiment with the preceding one, and remember the lesson which the two combined inculcate.

(*c*) *Groups III. and IV. from each other.*

106. Prepare a mixed solution of the chlorides of *cobalt*, *strontium*, and *magnesium*, and separate out the cobalt (after addition of some sal-ammoniac) by means of sulphide of ammonium, as shewn for iron in sect. 99. From the filtrate precipitate the strontium by adding excess of carbonate of ammonia, and heating. Filter off the carbonate, and prove the presence of magnesium in the filtrate by means of phosphate of ammonium. Take care to wash your precipitates properly.

The analytical methods given in the preceding sections may be translated in more than one way into a

SCHEME FOR THE EXAMINATION OF A SOLUTION OF MINERAL SALTS FOR THE METALLIC OXIDES CONTAINED IN IT.

The one which we recommend is as follows :

107. *Preliminaries.*—(*a*) Observe colour, smell, action on test-papers. (*b*) Evaporate a few drops on a strip of glass to dryness, and see if there is a solid residue. See if the residue disappears when exposed to a dull red-heat. Interpret your observations.

If the solution is alkaline or neutral, acidify a sample by gradual addition of dilute nitric acid, and if there is no change in the cold, heat to incipient ebullition. If a *permanent* precipitate is produced, this shews that most probably you have to deal with one of those cases *which our scheme does not take into account.*[*] If the solution remains or ultimately becomes clear, take a larger sample of the O. S.,[†] and by adding a sufficient excess of

108. *Hydrochloric Acid*, precipitate what may be present of the radicles of Ag_2O, Hg_2O, and PbO, as shewn for silver in sect. 97. (In any case enough of HCl must be added to produce a very decided acid reaction ; a transitory precipitate produced in an alkaline solution may consist of hydrates of ZnO, Cr_2O_3, Al_2O_3, or other insoluble oxides, present as alkali salts.) Collect the *silver-group* chlorides on a filter, wash them with small instalments of cold water, but take care to add only the more concentrated of the washings to the filtrate, which can be assumed to be quite free of Ag and 'mercurosum' (mercury present as Hg_2O), but may contain a trace of lead. [It is as well here to notice that $PbCl_2$ is far less soluble in hydrochloric acid than it is in pure water, while, on the other hand, $AgCl$, which is quite insoluble in water, dissolves appreciably in hydrochloric acid. Hence in searching for lead we should use a considerable excess of HCl, while in the case of

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[*] A few of these, however, will be noticed under the head of 'Detection of Acids.'

[†] Original solution.

silver we must restrict ourselves to the minimum of reagent required to supply the necessary chlorine.]

109. Test the filtrate for *nitric acid*, and if it is present, remove it as shewn in the exercise in sect. 97; dissolve the chloride-residue in water, and without heeding any precipitate that may be produced, precipitate the *copper* and *arsenic group* metals by means of

110. *Sulphuretted Hydrogen*, and separate the two groups from each other, as shewn in exercise, sect. 98.

From the filtrate now the *barium group* might at once be separated out by adding excess of sulphuric acid and heating—which brings down the BaO and SrO as sulphates—filtering off these, and, after due concentration, precipitating the lime by adding to the liquid half its volume of alcohol, and allowing to stand. The filtrate from the $CaSO_4$ is evaporated to about one-fourth of its volume to expel the alcohol, and the liquid then examined successively for the iron-group oxides, magnesia, and alkalies; but as a rule it is preferable to operate as follows:

From the filtrate (off the H_2S-precipitate) we next eliminate what can be precipitated by means of

111. *Sulphide of Ammonium* (operating, as shewn in exercise in sect. 99 for iron); we filter off and wash the precipitate, and thus obtain a filtrate which can contain only the barium-group oxides, magnesia, and alkalies.

112. The *Barium-group* metals are precipitated by means of excess of *carbonate of ammonia* in the heat, and filtered off, and a part of the filtrate is next tested for *magnesia* with phosphate of ammonia. The alkalies, if present, are in the last filtrate.

113. All that remains to be done now is to examine the several products for the individual metals that may be contained in them. But this problem we cannot profess in this little book to take up in its entirety; what we propose to do is, on the assumption that each of the several products contained only one metallic oxide, to shew how that one oxide can be identified. How far the methods to be given apply to more complex cases, the intelligent student will easily make out for himself. (For exhaustive methods, we

must refer to treatises on the subject, such as the author's *Manual of Analysis.*)

ANALYSIS OF THE SEPARATE GROUPS.

114. *The Silver-group Precipitate* is easily analysed, so easily that, for once, we may go beyond our programme, and proceed on the assumption of the three chlorides being present in it. Boil the precipitate with water, and filter hot. The

<table>
<tr><th>$PbCl_2$</th><th>AgCl</th><th>Hg_2Cl_2</th></tr>
<tr><td rowspan="3">Dissolves; the solution on cooling, deposits crystals of the chloride, if sufficiently strong.
H_2SO_4 gives a white precipitate of $PbSO_4$.</td><td colspan="2">Remain undissolved. Wash off all the $PbCl_2$, and then treat in the cold with <i>ammonia.</i></td></tr>
<tr><td>AgCl dissolves; when the solution is acidified, the whole of the AgCl is re-precipitated.</td><td>Hg_2Cl_2 is converted into a <i>black</i> insoluble compound.*</td></tr>
<tr><td colspan="2">Hg_2Cl_2, when treated with Cl_2 water, dissolves as $HgCl_2$. AgCl is insoluble in this reagent.</td></tr>
</table>

115. *The Copper-group Sulphides* can to some extent be distinguished by their colours, *and if properly washed,* by their different behaviour to acids.

<table>
<tr><th>HgS.</th><th>CuS.</th><th>(PbS).</th><th>Bi_2S_3.</th><th>CdS.</th></tr>
<tr><td>Jet black.</td><td colspan="3">Almost black.</td><td>Yellow.</td></tr>
<tr><td colspan="5"><i>When boiled with hydrochloric acid</i> (20 <i>per cent.</i>).</td></tr>
<tr><td>HgS remains unattacked.</td><td>CuS is hardly attacked.</td><td colspan="3">These sulphides are dissolved as <i>chlorides</i>, with evolution of H_2S.</td></tr>
<tr><td colspan="5"><i>When boiled with dilute sulphuric acid.</i></td></tr>
<tr><td colspan="4">These sulphides remain undissolved.</td><td>CdS dissolves as $CdSO_4$.</td></tr>
</table>

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* Hence the name of 'calomel,' from the Greek words *kalos* (beautiful) and *melas* (black).

Hence, by means of these acids, the group may be split up into three sub-groups, Cd; Bi and Pb; Cu and Hg; and the two metals named last can be separated by boiling with nitric acid, which dissolves all the sulphides named as nitrates except the HgS.

Supposing only *one* of the metals to be present in the original solution (or the solution obtained from the sulphide by means of acid),

116. (1) *Cadmium* is easily recognised by the yellow colour of its sulphide. O. S., when mixed with ammonia, gives a white precipitate of hydrate, soluble in excess of ammonia, into a *colourless* liquid.

117. (2) HgO-salt, when decomposed by gradual addition of H_2S, does not yield sulphide all at once, but first gives an almost white precipitate of $HgS + HgX$ ($X =$ Cl, NO_3, &c.), which, on further addition of reagent, gets more and more completely converted into HgS, and in consequence of this change, successively assumes a yellow, orange, brown, and at last a jet-black colour. The sulphide thus produced being very heavy, settles down like so much sand. The O. S., when mixed with *stannous chloride*, gives a white precipitate of *calomel*, which, when heated with excess of reagent, becomes gray or black from metallic mercury.

118. (3) Supposing now HgO and CdO are proved absent, then, to test for the three other metals, add to the original solution excess of ammonia. Salts of

CuO	PbO	Bi_2O_3
Give a green precipitate, soluble in excess of NH_3 into a dark blue liquid.	Give white precipitates of hydrate, insoluble in excess of ammonia. To discriminate, dissolve the washed hydrate in the *least quantity* of dilute nitric acid on the filter, wash down with water, and add *Iodide of Potassium.* Result:	
	Yellow precipitate of PbI_2.	Dark-brown precipitate of BiI_3.

Data for Confirmatory Tests

119. **Lead** is the only metal of this group which is precipitated by H_2SO_4.

120. **Bismuth** salts, if not entirely insoluble in water, are all decomposed by it, with formation of insoluble basic salts; this holds more especially for the chloride. To identify a Bi_2O_3 solution, add first ammonia, drop by drop, until a precipitate is formed which disappears very slowly on shaking; then dilute largely with water, and if no precipitate appears, add some chloride of sodium: the bismuth will be precipitated as a basic salt, which, if alkaline chloride was used, is always $BiOCl$.

121. **Copper** solutions give a deposit of *copper* on an iron wire placed in the solutions; this, however, holds only for acid solutions; not for instance, for the blue liquid produced by addition of ammonia. Acid solutions, however dilute, give a brown-red precipitate when mixed with ferrocyanide of potassium.

122. **The Arsenic-group Sulphides,** if produced by the action of sulphuretted hydrogen on pure solutions of the respective oxides, can be distinguished from one another, to a certain extent, by their colours and solubilities in the reagent solutions to be named.

As_2S_3	Sb_2S_3, Sb_2S_5	SnS	SnS_2
Yellow.	Orange red.	Dark-brown.	Yellow.
*Insoluble in	Readily dissolved by		
Boiling 20 per cent. hydrochloric acid, with evolution of H_2S and formation of			
	$SbCl_3$†	$SnCl_2$	$SnCl_4$
When the sulphides are treated with concentrated solution of *Sesquicarbonate of Ammonia*, at 80° C.			
As_2S_3 only dissolves; it is re-precipitated on acidification with HCl.	These sulphides remain undissolved, substantially at least.		

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* Remember that CdS, which looks like As_2S_3, is readily dissolved by the acid when hot.

† And S_2 in the case of Sb_2S_5.

Identification of

123. **Sulphide of Arsenic.**—Dissolve by heating with hydrochloric acid and a granule of chlorate of potash; the arsenic dissolves as *arsenic acid*, which behaves to magnesia mixture and to molybdate of ammonia as if it were orthophosphoric (comp. sect. 69). Filter off the sulphur, add excess of ammonia and then *magnesia mixture.* The AsO_4MgNH_4 precipitate will come down on standing.

124. To distinguish it from the P_2O_5 compound, place a little of the moist precipitate on one end of an *asbestos stick*, and heat it in the 'yellow' tip of the flame of a Bunsen, produced by partially shutting the draught-holes, taking care at the same time to hold the convex side of a Berlin basin into the flame, close above the sample. Metallic arsenic is formed, part of which deposits on the basin as a 'mirror,' insoluble in cold dilute nitric acid, soluble in bleaching-powder [$Ca(ClO . Cl)$] solution.

Or else dissolve the sulphide in pure nitric acid and apply the molybdenum test; the result is the same as in the case of P_2O_5, except that the precipitate is a little slower in coming out. A third method is to apply

125. *Marsh's Test*, which, in fact, may serve to identify any arsenic solution producible by dissolving As_2O_3 or As_2O_5 in water, or aqueous alkali or non-oxidising acids. The apparatus required is a gas-evolution bottle of, say, 300 c.c. capacity, provided with a funnel tube; the exit-tube should be connected with a cotton-wool tube to purify the gas to be evolved, and through it with a *hard* glass tube, 15 centimetres long, and 4—5 mm. wide inside, which must be drawn out into a fine point at the exit-end. Charge the flask with 20—30 grms. of *granulated zinc*, and by addition of 10 per cent. sulphuric acid (or 10 per cent. HCl), generate a current of hydrogen. When *all the air is expelled*, kindle the gas, and in order now to make sure of the purity of the reagents, heat a portion of the hard tube to redness, and after having kindled the gas, hold a porcelain crucible lid into the flame. If the hydrogen is pure, it will of course deposit nothing

either on the crucible lid or within the tube. Now pour in the (acidified) liquid to be tested through the funnel tube. The arsenic, if present, will come off as arseniuretted hydrogen, AsH_3 (along with a large excess of free H_2), which will be decomposed, partly in the red-hot tube with formation of a *mirror* of metallic arsenic, the rest wholly in the flame; and the latter consequently will now deposit *stains* of metallic arsenic on the porcelain. This test is extremely delicate, but not absolutely characteristic, as antimony solutions behave quite similarly to nascent hydrogen as arsenic ones do. But the two kinds of stains are easily distinguished.

126. The *arsenic* stains are bright and metallic-looking; they readily dissolve in bleaching-powder solution. Antimony *stains* (generally) are dull, sooty-looking; they do not dissolve in the hypochlorite solution.

Either stain, when heated with yellow sulphide of ammonium, dissolves, and the liquid, on evaporation, leaves a residue of metallic sulphide. But while arsenic sulphide is yellow, the antimony sulphide formed (in this case) has a brick-red colour, and it readily dissolves in a drop of cold fuming hydrochloric acid.

127. The arsenic *mirror*, when the portion of the tube which contains it is heated in a dry test-tube, is oxidised into white arsenic, which forms a sublimate in the test-tube, consisting of colourless, sparkling crystals, slowly soluble in hot water.* The

128. **Aqueous Solution** of As_2O_3 obtained exhibits the following reactions: It is only feebly acid to litmus. H_2S gives a yellow *coloration;* a precipitate of As_2S_3 appears only on addition of HCl. *Nitrate of silver* (generally) produces no change; but when the mixture is very cautiously neutralised with (dilute) ammonia, a yellow precipitate of AsO_3Ag_3 comes down.

129. *To distinguish the Chloride Solutions of* **Antimony and Tin**, as produced by boiling the respective sulphides with hydrochloric acid, remove the bulk of the excess of

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* Regarding the antimony mirror and other methods of discrimination, see the author's *Manual.*

acid by evaporation, or cautious addition of carbonate (or hydrate) of soda-solution; then place the liquid in a platinum basin, and drop in a granule of zinc. Both metals are precipitated as metals. But while the *tin* forms a metallic-looking crystalline deposit, which, after removal of the mother liquor and excess of zinc, dissolves in hot hydrochloric acid as $SnCl_2$; the antimony always appears as a dull, sooty-looking deposit on the platinum, which is almost insoluble in hot hydrochloric acid.

The stannous chloride solution obtained can be identified by means of mercuric chloride, which produces in it a white precipitate of calomel. It is as well to observe that this is not a test for tin, *quâ* tin, but a test for a certain class of reducing agents, including stannous salts.

130. *Appendix on* **Arsenic Acid.**—A purely aqueous solution of this acid acts strongly on litmus. It gives no precipitate with sulphuretted hydrogen. But when hydrochloric acid is added besides the H_2S, the arsenic acid, on standing, is very slowly reduced to As_2O_3, with precipitation of sulphur, which, however, gets mixed with the As_2S_3, produced from the As_2O_3 by the excess of reagent. If there is enough of H_2S, the arsenic, after 24 or 48 hours, is completely precipitated as a kind of pseudo-pentasulphide—that is, as a mixture of $As_2S_3 + S_2$. This process goes on far more quickly at a temperature of 70—80° C. than in the cold.

131. Before passing on to the *Sulphide of Ammonium Precipitate*, let us remind the student of the quasi-exceptional reactions on sulphuretted hydrogen in the presence of free acid, of solutions of the oxides CrO_3, Mn_2O_7, Fe_2O_3. Such solutions, when treated with this combination of reagents, give precipitates of *sulphur* with formation of solutions of salts of Cr_2O_3, MnO, FeO respectively. These reductions are accompanied by characteristic changes of colour. Solutions of CrO_3 are intensely yellow or garnet-red; those of Mn_2O_7 still more intensely purple; ferric-salt solutions are not necessarily coloured, but they become intensely yellow (from $FeCl_3$) when heated with hydrochloric acid. On the other hand, solutions of Cr_2O_3 salts are violet

or green;* those of MnO and FeO salts are colourless—even in the heat and in the presence of free hydrochloric acid.

132. Let us now assume the solution to be analysed had either failed to act on H_2S, or had been exhaustively treated with this reagent in the presence of hydrochloric acid, and the precipitate formed been filtered off. In this case, as in any other, we begin by noticing the colour of the liquid. Solutions of

(1) FeO, MnO, ZnO, Al_2O_3 are colourless.

(2) NiO: green (not very intense).

(3) CoO: pink (more intensely so than NiO ones are green); when heated with fuming hydrochloric acid, they become very intensely blue.

(4) Cr_2O_3: intensely green or violet; so intensely, that a *colourless* solution may at once be put down as *not* containing any chromium.

133. We next neutralise a portion of the liquid with ammonia, and add excess of sulphide of ammonium, and observe the colour of the precipitate:

(1) CoS, NiS, FeS are black.

(2) $Cr_2(OH)_6$: green or violet.

(3) MnS: flesh-coloured when quite pure; when slightly impure, dirty white or gray; becomes *brown* by oxidation on exposure to air. Occasionally, especially when produced in the heat, the manganese precipitate exhibits a *green* colour.

(4) $Al_2(OH)_6$ is a gelatinous, semi-transparent colourless precipitate.

(5) ZnS is white.

134. Supposing for a moment we had to deal with a *mixed* precipitate, we need only collect and wash it, and then treat it in the cold with 5—10 per cent. HCl,† as shewn in Exercise 92, and we split up the mixture into two parts, separable by filtration—namely:

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* The violet ones become green on boiling.

† In the absence of foreign groups and oxydising agents, the HCl may be added to the unfiltered mixture.

(A) *CoS and NiS*, which remain substantially undissolved; and

(B) The rest of the metals which pass into solution as chlorides;[*] and

135. Group B, again, might be split up into two parts, as follows: Boil the solution with a little chlorate of potash; the ferrous salt only is oxidised (into ferric salt), which is at once recognised, in originally colourless solutions, by its intensely yellow colour; *vide supra*), so that we have to deal, in general, with a mixture of sesquioxides, Fe_2O_3, Cr_2O_3, Al_2O_3, and protoxides, MnO, ZnO. To separate these from each other, add to the cold dilute liquid (sal-ammoniac, if necessary, and) ammonia, drop by drop, until the mixture is strongly alkaline. The effect on simple solutions is as follows:

The sesquioxides are precipitated as hydrates. $Fe_2(OH)_6$ is a *brown* precipitate.	*The protoxides* remain dissolved. The *MnO* solution absorbs oxygen from the air, and becomes turbid from a brown hydrate of Mn_2O_3. The ZnO solution remains clear.

In the case of a mixed solution, to effect an (approximate) separation, boil off the free ammonia—that is, boil until the vapours no longer smell of NH_3, and filter:

Precipitate.—The sesquioxides + traces of the protoxides.[†]

Filtrate.—MnO and ZnO only. The MnO solution *now* no longer absorbs oxygen from the air. H_2S precipitates almost all the Zn as ZnS, but no manganese.

136. We will assume now the O. S., or the solution derived from the sulphide of ammonium precipitate by treatment with acids, contained only one of the oxides of the *iron group*. In this case, what we have learned, enables us to discriminate between all the different oxides; hence we may pass to giving data for

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[*] If no H_2S were produced, this would prove the absence of all the sulphides; comp. sect. 95.

[†] Consult sect. 144.

CONFIRMATORY TESTS.

137. **Cobalt.**—The sulphide dissolves in hydrochloric acid and chlorate of potash (or in aqua regia) in the heat as chloride. The solution (or O. S.) shews the following reactions: NH_4Cl and ammonia in excess: formation of a brown solution, which absorbs oxygen from the air, and becomes red. Concentrated solutions, when mixed with excess of *nitrite of potash*, and then acidified with acetic acid, gradually deposit 'cobalt yellow' (a double nitrite of Co_2O_3 and K_2O). Remember the *borax-bead* test given in Exercise 11.

138. **Nickel.**—The sulphide is appreciably soluble in excess of *yellow* sulphide of ammonium, with formation of a *brown* filtrate: a very characteristic reaction which, however, frequently fails to come out when the precipitated sulphide of nickel is associated with other sulphides. Its solubilities are otherwise the same as those of the cobalt compound. *In solutions of salts:* Sal-ammoniac and ammonia produce a *blue* liquid, permanent in air. *Nitrite of potash*, &c.: negative result. *Borax bead:* quite different from the cobalt one. See sect. 11.

139. **Chromium.**—Regarding this metal, we refer to what has already been said, and to sects. 11 and 23.

140. **Manganese.**—See sect. 133 (3); and sects. 11 and 22.

141. **Zinc.**—The sulphide is white, and does not change colour in air. To further identify it, place a little of the precipitate on one end of an asbestos stick, 'roast' it over a Bunsen, moisten with a drop of cobalt solution, heat strongly, and allow to cool: a *green* compound of ZnO and Co_2O_3 will be obtained. Comp. sect. 15.

142. **Iron** as FeO or Fe_2O_3 is easily identified by the methods given. The following tests enable one to discriminate between ferrous and ferric salt solutions:

Reagent.	FeO Salts.	Fe_2O_3 Salts.
Sulphuretted hydrogen.	No change.	Precipitate of sulphur.
Ferrocyanide of potassium.	White precipitate.	Blue precipitate.
Ferricyanide of potassium.	Blue precipitate.	Brown coloration.
Sulphocyanate of K or NH_4.	No change.	Deep blood-red colour.

143. **Aluminium.**—Pure alumina is a white solid, which, when heated on charcoal in a blow-pipe flame, remains absolutely unchanged. When moistened with cobalt solution, and then again heated strongly in an oxidising flame, it is converted into a compound of Al_2O_3 and CoO, which, *after cooling*, is blue. Many infusible alumina compounds—for example, kaoline (clay)—behave so far like alumina itself.

Solutions of alumina salts, when mixed with caustic potash or soda, give a precipitate of alumina which is soluble in excess of reagent. From the solution the alumina is reprecipitated by addition of sal-ammoniac—that is, by replacement of the potash or soda by ammonia. This latter reaction serves to distinguish alumina from oxide of zinc, which, like the former, is soluble in fixed caustic alkali, but unlike it, soluble also in ammonia.

144. **Appendix.**—Besides the substances which we took into account in the general sketch of our scheme, a sulphide of ammonium precipitate is liable to contain a number of salts of baryta, strontia, lime, magnesia, which, while soluble in acids (for example, HCl or HNO_3), are insoluble in water, and not decomposed by ammonia, nor by the ammonia potentially present in sulphide of ammonium. Acid solutions of this class of salts (of which *phosphate of lime*, *phosphate of ammonia and magnesia*, and *oxalate of lime* may be mentioned as being of comparatively frequent occurrence) behave to ammonia and sal-ammoniac like those of alumina; but unlike these, when heated with excess of caustic alkali, they give permanent

precipitates: phosphate of lime being precipitated as such, the magnesia salt yielding a precipitate of hydrate, $Mg(OH)_2$. The latter, when dissolved in hydrochloric acid, is not reprecipitated by ammonia.

The insoluble barium-group salts [for example, $(PO_4)_2Ca_3$] are recognised, as compounds of that group of bases, by their giving a precipitate of sulphate on addition of sulphuric acid and alcohol to their solutions.

145. *The Carbonate of Ammonia Precipitate* must in general be looked upon as a mixture of the carbonates of barium, strontium, and calcium.

146. To search for *barium*, dissolve the precipitate in acetic acid, and add bichromate of potash: the baryta only is precipitated—as a pale-yellow precipitate of $BaCrO_4$, which is readily identified by the flame test (given in sect. 5). From the filtrate, the

147. *Strontium* can be precipitated by addition of excess of sulphuric acid, and heating. After filtering off the $SrOSO_3$, the calcium can be precipitated by means of carbonate of ammonia. But this method of separation is not exact, hence the $SrSO_4$, as well as the $CaCO_3$, must be identified by special tests.

METHODS OF IDENTIFICATION.

148. **Barium** (*vide supra*).

149. **Strontium** compounds are identified by the flame test, which, however, if lime is not sure to be absent, had better be confirmed by means of the spectrum apparatus.

150. **Calcium.**—A dilute solution of calcium salt, when mixed with sulphuric acid, gives a precipitate of sulphate only in the presence of alcohol. To make sure of the identity of the precipitated sulphate, filter it off, wash it two or three times with fifty per cent. alcohol, and then with *hot water;* the aqueous filtrate contains enough of CaO to give a distinct precipitate with *oxalate* of ammonia, which reagent, by the way, is the most delicate of calcium precipitants.

151. *The filtrate from the Barium-group Precipitate* can

contain no other metallic salts than such of magnesia, potash, and soda. To test for magnesia, add to a portion phosphate of ammonia and free ammonia, stir up violently, and allow to stand (for some hours if necessary). A precipitate formed consists of PO_4MgNH_4, and, if we filter it off, the potash and soda are in the filtrate.

152. To extract them, add a quantity of pure *milk of lime*, which must be sufficient to decompose the ammonia salts present, and to precipitate all the P_2O_5; boil down until the vapours no longer smell of NH_3, then add a few drops of ferric chloride, and—after having made sure that the liquid is still strongly alkaline to turmeric —filter off the precipitate [$Ca(OH)_2$, $(PO_4)_2Ca_3$, PO_4Fe]. From the filtrate precipitate the lime by carbonate of ammonia in the heat, filter, and evaporate the filtrate to complete dryness. Place the residue in a platinum crucible, and in it keep it at a dull red-heat, until the ammonia salts are driven off. The residue should, by theory, consist of soda and potash salts only. Practically, it will, as a rule, not prove quite pure, but on being treated with a small quantity of water, leave a residue. Filter off the impurities, add a few drops of carbonate of ammonia, heat, filter again, and evaporate the filtrate to dryness a second time, and, if a residue remains, subject it to the flame test (Exercise 5). If the flame-colour produced is *violet*, this proves the presence of potash and the substantial absence of soda. If the flame is *yellow*, this proves the presence of soda (which, however, may only amount to a mere trace), but it does *not* prove the absence of potash. The spectrum apparatus enables one to see the potash beside the soda rays. In any case it is as well to confirm the result by the wet-way tests to be given presently.

153. *Examination of a salt known to contain no bases except* K_2O, Na_2O, *or* $(NH_4)_2O$.—Heat some to dull redness; the NH_3 (although not necessarily the ammonium salt as a whole) goes off completely, so that the residue can contain only potash and soda. To test for potash :

154. *First Method.*—Dissolve in a *very little* water;

acidify, if necessary, with acetic acid; add *bitartrate of soda*, and stir up violently. The potash, if present, comes down gradually as 'cream of tartar,' $C_4H_4O_6 . KH$.

155. *Second Method.*—Dissolve in a very little water, and if the solution is alkaline, acidify slightly with hydrochloric acid; if not, add a drop or two of concentrated solution of NaCl, and then concentrated chloride of platinum, and allow to stand. The potassium, if present, is precipitated (slowly) as chloroplatinate, $PtCl_6K_2$. The second method is utterly inapplicable,* the first is not safe, in the presence of ammonia salts.

Satisfactory wet-way tests for *soda* are not known.

156. **Ammonia** must always be searched for in the O. S. For this purpose add excess of caustic soda, and heat gently. If ammonia salts are present, NH_3-gas is set free, which is recognised:

(1) Comparatively large quantities: by the characteristic pungent odour of the gas.

(2) Lesser quantities: by its characteristic action on turmeric-paper.

(3) The least traces by *Nessler's Reagent* or mercuric chloride.

(*a*) *Nessler's Reagent* (a solution of the double salt $HgI_2 + 2KI$ in aqueous caustic potash or soda).—This reagent produces in even the most dilute solution of free ammonia, or of *pure* (NH_4) salts, a brown precipitate, or at least a brown coloration, of a compound, $N_2Hg_4I_2 + 2H_2O$.

(*b*) *Mercuric Chloride.*—Very dilute solutions of this reagent are not precipitated by carbonate of soda; but when the solution contains ever so little of an ammonia salt, the carbonate of soda produces a white precipitate of the chloride of a mercurammonium.

Neither of these two tests (*a* and *b*) should be applied to complex solutions. From such the ammonia must be eliminated by distillation with caustic alkali, and searched for in the distillate.

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* Ammonia salts behave to chloride of platinum like potash ones. The precipitate $PtCl_6(NH_4)_2$ looks like the K compound.

INSTRUCTION FOR THE DETECTION OF THE MORE COMMONLY OCCURRING NON-METALLIC ACIDS.

157. There is no *convenient* method known, by means of which even the small number of acids which we propose to take into account (supposing them to occur together in a given solution) could be *divided analytically* into groups, which might then be split up separately into their respective members. What we must do, therefore, is merely to arrange the acids in our mind into groups in such a manner that each group is within the range of a certain general reagent, and then, in each analysis, to successively apply these reagents to separate portions of the original solution.

158. The mode of classification which we propose to adopt is as follows :

GROUP I.—'VOLATILE' ACIDS.[*]

	Formula of	
Name.	Hydrogen Salt.	Characteristic Volatile Product.
Carbonic	H_2CO_3	CO_2
Sulphhydric	H_2S	H_2S
Hydrocyanic	HNC	HNC
Sulphurous	H_2SO_3	SO_2
Thiosulphuric	$H_2S_2O_3$	SO_2
Nitrous	HNO_2	NO
Hypochlorous	$HClO$	Cl_2O or Cl_2

Group Reagent.—Dilute sulphuric, or other mineral, acid.

GROUP II.—'HALOGEN' (including Cyanogen) ACIDS.

(*A*) Hydrochloric, HCl ; Hydrobromic, HBr ; Hydriodic, HI ; [Hydrocyanic, HNC] ;[†] Ferrocyanic, $H_4Fe(NC)_6$; Ferricyanic, $H_3Fe(NC)_6$; Sulphocyanic, $HNCO$.

(*B*) Iodic, HIO_3 ; Bromic, $HBrO_3$.

(*C*) Chloric, $HClO_3$; [Hypochlorous, $HClO$].

Group Reagent.—Nitrate of Silver.

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[*] That is, acids which, when liberated within a dilute aqueous solution, furnish gaseous products which can be liberated from the solution without the application of high temperatures. Hence muriatic acid, for instance, is not what we here call a volatile acid.

[†] The bracket means : 'Already named under a previous heading.'

GROUP III.—SULPHUR ACIDS.

(*A*) Sulphuric, H_2SO_4.
(*B*) (Sulphurous, H_2SO_3; Thiosulphuric, $H_2S_2O_3$).

Group Reagent.—Chloride (or Nitrate) of Barium.

GROUP IV.

Orthophosphoric, H_3PO_4 (and Arsenic, H_3AsO_4).

Group Reagent.—Magnesia Mixture.

GROUP V.

Oxalic (and Phosphoric).

Group Reagent.—Chloride of Calcium.

GROUP VI.

Nitric, HNO_3; (Nitrous, HNO_2).

Group Reagent.—Ferrous Sulphate.

GROUP VII.—BORIC ACID.

GROUP VIII.—SILICIC ACID.*

GROUP IX.—'ORGANIC' ACIDS.

(That is, compounds of the radicle, COOH.) Only a few of this very numerous class will be considered individually.

Instruction.

159. Supposing for a moment the substance to be examined were a *solid salt.* In this case we begin by studying its behaviour (1) when heated, and (2) when treated with *concentrated sulphuric acid*, and note the effects.

160. (1) *When heated* (on platinum foil), *most organic acid* salts yield black charcoal, and, in the presence of alkalies or BaO, SrO, CaO, as bases, even those that do not, leave a residue containing *carbonate*, and consequently giving off CO_2 on addition of an acid.

Chlorates, also nitrates, give off *oxygen*-gas, recognisable by the well-known glowing-splinter test. In the treatment with

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* Hydrofluoric should come in between VIII. and IX., as an acid of very common occurrence in minerals; but we do not intend to consider it.

161. (2) Concentrated sulphuric acid, which should first be applied cold, then hot, there is :

[*Oxygen evolved:* From permanganates, chromates, peroxides.]

Chlorine: From chlorides + oxydising agents.

Peroxide of Chlorine: A deep yellow gas: from chlorates. Action violent ;[*] Mixture yellow.

Iodine Vapours: From iodides, and from (iodates + reducing agents).

Bromine Vapours: (Brown) from bromides and bromates.

Muriatic Acid Fumes:[†] From muriates.

Nitrous Fumes: (Brown) from nitrites; on addition of copper, also from nitrates.

CO_2: From carbonates.

$CO_2 + CO$: From oxalates.

[CO pure: From formates.]

Charcoal and gases: From many organic compounds.

162. After these preliminaries we must bring the substance (or the acids contained in it) into solution, so that the acids remain undecomposed and are *not* associated with inconvenient bases. Regarding the methods to be used for this purpose, we refer to the author's *Manual.* Supposing the solution or solutions to be prepared, we apply to them successively the several group reagents named in our list, in the order in which they are there enumerated. We accordingly begin by searching for *volatile acids* by means of

I. DILUTE MINERAL ACID.

163. We generally prefer sulphuric, because it is absolutely non-'volatile,' but occasionally substitute hydrochloric or nitric, to avoid the formation of *precipitates* of sulphates or chlorides (such as $BaSO_4$, AgCl, &c.). In applying this reagent, remember that the object is to liberate the acid sought for, which necessitates the use of a considerable excess of reagent. If there is no visible effect in the cold, apply a gentle heat. Besides searching for the volatile products named in sect. 158, look for a precipitate in the mixture. A precipitate of

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[*] Beware of explosions !

[†] See sect. 32.

(1) White milky *sulphur* indicates polysulphide, such as $K_2S \cdot S$.

(2) *Yellow Sulphur:* thiosulphate.

(3) '*Silica*'—a gelatinous white or colourless precipitate: alkaline silicate. But the non-appearance of a silica-precipitate does not prove the *absence* of silicate. The volatile products to be looked for are:

164. (1) *Carbonic Acid*, CO_2.—This product, when liberated in quantity, effervesces away as a colourless, inodorous gas, precipitating lime-water (sect. 55). Small quantities remain dissolved in the liquid, and must be eliminated either by a short ebullition, or by means of hydrogen generated within the liquid by adding a piece of zinc.* The CO_2 liberated by either means must be passed through the lime-water by means of a gas-evolution tube, adapted to the reaction-vessel. Baryta-water is a more delicate reagent for CO_2 than lime-water, but it is liable to become turbid from SO_2 and (mechanically carried over) sulphate.

165. (2) *Sulphuretted Hydrogen.*—Large quantities effervesce off; but even when there is not enough of the gas formed to cause an effervescence, some of it soon gets diffused through the atmosphere of the test-tube, and there can easily be detected and recognised by its smell and action on lead-paper (comp. sect. 74).

166. (3) *Hydrocyanic Acid* never comes off with effervescence; but readily diffuses out of the liquid into the air even in the cold; the least traces being readily detected and recognised by its characteristic odour, which, if the quantity is not very minute, is accompanied by a peculiar sensation in the back of the mouth.† Of *chemical* tests the following two may be named:

167. (*a*) Liberate the NCH by addition of dilute H_2SO_4 (not by HCl) in a beaker, and cover the latter with glass plate, to which a drop of nitrate of silver has previously been attached. The NCH liberated gradually collects in the silver solution, and produces a turbidity of cyanide of silver.

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* In this case, if lower sulphur acids than H_2SO_4 are present, H_2S is evolved.

† Hydrocyanic acid being dangerously poisonous, the verification of the above statements should be effected with very dilute solutions, prepared by the teacher for the purpose.

(*b*) Or else: collect the NCH in a drop of caustic soda lye, spread over the glass plate, as cyanide of sodium, and identify the latter by means of the Prussian-blue test, to be given in sect. 176.

168. (4) *Sulphurous Acid.*—No effervescence in the cold, and not even on gentle heating, unless the solution is exceptionally highly concentrated. The gas readily escapes from the mixture by diffusion; it is recognised by its smell and by its decolourising a paper moistened with permanganate of potash.

169. (5) *Nitric Oxide* is liberated from sufficiently concentrated solutions of nitrites. Forms red fumes of N_2O_4 in the air. Small quantities of nitrous acid liberated within much water remain undecomposed, but can be recognised by the reactions to be given in sect. 188.

170. (6) *Chlorine*—liberated from mixtures of hypochlorites and chlorides, such as bleaching-powder, is recognised by its yellow colour (when not too largely diluted with air); by its characteristic smell, and by its power of bleaching moist litmus and indigo paper; the least traces: by means of iodide-of-potassium-and-starch paper, which becomes blue when brought in contact with chlorine.

II. NITRATE OF SILVER.

171. This reagent, as already stated, serves chiefly for the detection of the *halogen acids.* But before applying it for that purpose, it is as well to use it as a reagent for sulphide and thiosulphate, either of which might possibly have escaped detection in Operation I.

172. *Sulphide solutions* (with the reagent) give black precipitates of sulphide of silver, insoluble in alkalies (including ammonia), and insoluble in cold dilute nitric acid.

173. *Thiosulphate* solutions give white precipitates of $Ag_2S_2O_3$ (soluble in excess of alkaline thiosulphate), which, when the mixture is heated, break up into sulphide of

silver and sulphuric acid : $Ag_2S_2O_3 = Ag_2S + SO_3$. Assuming now these two classes of salts to be *absent*, then to test for

174. *Sub-groups A and B*, acidify some of the O. S. with nitric acid (if necessary), add nitrate of silver in excess, and then more nitric acid. A *permanent* precipitate contains what is present of A or B, as silver salts ; the filtrate (besides more or less of the bromate, which is never completely precipitated) contains the sub-group C (and possibly many other acids besides).

If A or B were found *present*, next test samples of the O. S. as follows, for the

175. (1) *Complex cyanogen acids* by means of ferric chloride and ferrous salt, according to sect. 142. In the case of a negative result,* test for (simple)

176. (2) *Cyanides* as follows : Add to the O. S. (1) caustic soda in excess, (2) ferrous salt, (3) excess of hydrochloric acid, (4) ferric salt. If cyanides were present, there is formed a *blue* precipitate (or green coloration) of *Prussian blue*, $(NC)_6Fe . fe_4$; 'fe' $= \frac{1}{3}Fe''' = \frac{56}{3}$ parts of 'ferricum.' In the absence of NCH, search

177. (3) For *Iodides and Bromides* by means of *chlorine* water (which must *not* be applied to *alkaline* solutions). The respective radicles, if present, are eliminated as I_2 and Br_2 respectively, which, if the solution was dilute,† remain dissolved, imparting to the solution a brown or yellow colour. When the liquid is shaken with *bisulphide of carbon* (or *chloroform*) the halogen passes into the bisulphide (or chloroform), imparting to it, if the halogen is I_2, an intense violet colour ; if Br_2, a somewhat less intense yellowish-red colour.

Another reagent for distinguishing the two halogens is *starch* solution, which, when added to *free iodine*, strikes an intense blue colour ; (bromine solutions become yellow).

178. *Special Tests for Iodides.*—The silver salt is insol-

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* The other side of the alternative we cannot afford to consider.

† *Iodine* may separate out as a heavy black precipitate.

uble in ammonia; all other silver precipitates (except Ag_2S) are soluble in this reagent. *Nitrous acid* (produced in the O. S. by adding first nitrite of potash and then excess of dilute sulphuric acid) liberates *iodine*, which can be recognised as above. Hydrobromic acid is not decomposed by N_2O_3. Free iodine, as liberated from iodides by Cl_2, is *decolourised* by addition of excess of chlorine, being transformed thereby into iodic acid, which does not act visibly on starch nor on bisulphide of carbon or chloroform.

179. (4) *Bromates and Iodates* are easily distinguished from the corresponding haloids by their not giving free halogen with chlorine water, but doing so on cautious addition of sulphurous acid to the previously acidified solution. Excess of reagent takes away the free halogen by converting it into HI or HBr respectively.

If all these tests (sects. 175 to 179) give negative results, although the group A + B was proved to be present, the solution must contain *chloride.*

180. We will now proceed to shew how *Sub-Group C* can be detected in the presence of *chloride.* Acidify the O. S. with nitric acid in the cold, and by addition of nitrate of silver in excess and filtration, eliminate the *chloride*-chlorine. To the filtrate add excess of sulphurous acid, and heat; the Cl both of the HClO and $HClO_3$ is now precipitated as AgCl, mixed with more or less of sulphite of silver, which, however, is readily removed by heating the precipitate with dilute nitric acid.

181. The discrimination of the two acids 'C' offers no difficulty. Hypochlorite solutions, even if alkaline, decolourise *indigo-solution* in the cold. Chlorate solutions do not, not even after acidification with sulphuric acid; but when sulphurous acid is added to the blue mixture, the colour disappears through reduction of the $HClO_3$ to HClO.

182. *Appendix.*—Of nitrate of silver precipitates *soluble* in nitric acid, the following may be mentioned as possessing characteristic properties:

The orthophosphate, Ag_3PO_4	Yellow.
„ arsenate, Ag_3AsO_4	Brown-red.
„ arsenite, Ag_3AsO_3	Egg-yellow.
„ chromate, Ag_2CrO_4	Red.
„ oxide, Ag_2O	Dark brown.
„ sulphite, Ag_2SO_3	White, rather difficultly soluble in HNO_3.

III. CHLORIDE OF BARIUM.*

183. There is a great number of acids which from *neutral* solutions of their salts are precipitated by chloride of barium, but only one of the baryta salts thus producible is insoluble in aqueous mineral acids—namely, the *sulphate.* (Compare sect. 29.)

184. *Sulphurous* can be oxidised into sulphuric acid by the action of *iodine* [solution of iodine in iodide-of-potassium solution; the (brown) I_2 is reduced to (colourless) iodide], and by many other oxydising agents; also by the method given in the following sect. for

185. *Thiosulphate.*—To convert thiosulphate into sulphate, add excess of pure caustic potash,† and excess of permanganate, and heat. The reagent is reduced to hydrated binoxide, which is precipitated. To reduce the excess of Mn_2O_7(or MnO_3)K_2O, add a few drops of alcohol, and heat. Filter. The filtrate contains all the sulphur of the original thiosulphate as sulphate.‡

Iodine is decolourised by thiosulphate in neutral solutions, as also in the presence of free acid or of alkaline carbonate, with formation of tetrathionate, $R_2S_4O_6$, which does not precipitate $BaCl_2$.

IV. MAGNESIA MIXTURE

186. (As explained in sects. 69 and 70) is a delicate and characteristic precipitant for *orthophosphoric* and *arsenic acids.* Regarding discrimination, consult sect. 130.

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[*] Or nitrate, if the solution contains silver-group oxides.

[†] Even the commercial alkali, as a rule, is free from, while most kinds of caustic *soda* are contaminated with, sulphate.

[‡] Applies to all lower sulphur acids (except $S_2O_6H_2$?).

V. CHLORIDE OF CALCIUM,

187. From neutral or alkaline solutions, precipitates *phosphoric*, arsenic, arsenious, *oxalic*, *carbonic* (and also a number of other organic) acids. The *phosphate* is gelatinous; it dissolves in *acetic* acid.

The *oxalate* is powdery, and has the highly characteristic property of being insoluble in acetic acid. To identify precipitated oxalate of lime (or any other oxalate), boil with dilute sulphuric acid, and then add permanganate of potash; the oxalic is oxidised into carbonic acid, which escapes as CO_2, while the reagent is decolourised, being reduced to manganous salt.

VI. FERROUS SULPHATE

Is used for the detection of nitric and nitrous acid.

188. To detect *nitrite* (in a solution) add a slight excess of *dilute* sulphuric acid, and then saturated solution of the reagent; NO is produced, which dissolves in the ferrous solution with production of a black coloration. Even the most dilute solutions of nitrites, when acidified by dilute sulphuric acid, decolourise *permanganate*, and liberate *iodine* from iodide-of-potassium. The same tests when applied to

189. *Nitrate* give negative results. But the black nitric-oxide compound can be produced by adding to the O. S. first its own volume of *vitriol*, and then (after cooling) pouring the group reagent on the top of the mixture. The vitriol virtually takes away the water, and leaves real HNO_3 which then acts on part of the ferrous salt with formation of ferric salt, and of NO which dissolves in the ferrous layer and produces the colour.

VII. BORATES.

190. The solutions of the ordinary alkaline borates have an alkaline reaction like one of carbonate. On addition of hydrochloric acid, boric acid is set free, which is detected

by drenching a piece of turmeric-paper with the mixture, and drying it at a gentle heat, when it assumes a dark brown-red colour. But hydrochloric acid alone produces a somewhat similar effect; hence this test should always be accompanied by a *blank experiment.*

To identify a solid borate, treat it with oil of vitriol in a basin, add alcohol, and then set fire to the mixture. The borate of ethyl vapours produced cause the flame to exhibit a *green* colour.

VIII. SILICATES.

191. Anhydrous silica, SiO_2, is absolutely—the precipitated hydrates are relatively—insoluble in all acids except hydrofluoric. It is absolutely infusible; but when fused up with a carbonate soda bead, it readily dissolves in the reagent, with evolution of CO_2, and formation of a glass which, if it contains a sufficiency of SiO_2, *remains clear* on cooling.

Alkaline silicates dissolve in water with formation (in general) of alkaline liquids. These, when mixed with excess of hydrochloric acid, are decomposed with liberation (but not necessarily with *precipitation*) of silica. Evaporate to dryness, and re-dissolve in water: the whole of the silica now remains undissolved.

The student should assume our 'Instruction for the Detection of Acids' to terminate here, and before going further should practise both it and that given before for bases; first, with a selection of substances of known, and then with a greater variety of substances of unknown composition selected for him by his teacher. This system he must continue until he has completely mastered the whole of what we have attempted to teach him in the way of methods of salt analysis. He may then pass on to the following exercises on

IX. ORGANIC ACIDS.

(Compounds of COOH.)

Of this very numerous family (which includes several hundred members) only two—namely, carbonic and oxalic acid —were noticed in our 'Instruction.' We selected these two because, besides being of very frequent occurrence, they are almost the only ones for the detection of which it is possible to give straightforward rules of anything like general applicability. The following exercises on *tartaric* and *acetic acid* are meant to illustrate generic methods for the detection of organic acids generally, the former having been chosen as a representative of the non-volatile, the latter as one of the volatile members of the family.

192. Take a crystal of *tartaric acid*, $C_4H_6O_6 = (C_2H_4O_2)(COOH)_2$, and heat it on a piece of platinum foil. The acid first melts, and is then decomposed with evolution of inflammable gases, and formation of a *black* residue of charcoal, which latter, when heated in air, burns away completely (into CO_2).

193. Heat a fragment of tartaric acid (or any tartrate) in a dry test-tube with oil of vitriol. The acid undergoes a complete decomposition, with formation of a black semi-fluid mass containing charcoal, and evolution of CO_2, SO_2, and other gases.

194. Dissolve a few decigrams of tartaric acid in water, and neutralise the solution *partially* with *caustic soda*, *potash*, or *baryta*. Evaporate to dryness, and heat the residue in a close crucible, as long as any volatile products are seen to go off. Examine the residue. You will find it to consist of (black) charcoal mixed with the *carbonate* of the base employed; the latter is readily identified by addition of hydrochloric acid and identification of the CO_2 evolved.

195. Repeat the last exercise with *acetic acid* and baryta. The ignited residue this time is not black, but, as before, contains all the baryta as *carbonate*.

Queries: How would you test for organic acids in a mixture of salts known to contain carbonates? Anent 194, why did we recommend *partial* saturation?

196. Place 1—2 grms. of *acetate of soda* in a retort connected with a condenser; add a slight excess* of 20 per cent. sulphuric acid, and distil as long as drops of distillate come over; best out of an oil-bath kept below 130° C. Then add to the residue a little water and resume the distillation. The distillate contains the acetic acid of the salt as such, mixed of course with much water. This, bating certain limitations, is a general method for the isolation of volatile acids, and their separation from non-volatile ones. Of *inorganic* volatile acids which might pass into the distillate, hydrochloric and nitric are the most common. These, if present, may be removed by re-distilling the distillate after addition of excess of sulphate of soda. What excess means, follows from equation $Na_2SO_4 + HCl = NaCl + NaHSO_4$. Try this method with your distillate after having contaminated it expressly with a little hydrochloric acid. Keep the purified distillate for the specific tests to be given in sect. 200.

Identification of individual Acids.

ACETIC ACID, $CH_3 . COOH$.

197. Procure specimens of (*a*) glacial acetic acid; (*b*) acetate of potash; (*c*) crystals of acetate of soda, $C_2H_3NaO_2 + 3H_2O$; (*d*) crystals of 'sugar of lead' $(C_2H_3O_2)_2Pb + 3H_2O$, and familiarise yourself with their general properties.

198. Place 1—2 grms. of *acetate of soda* in a silver dish (as used for the Cr_2O_3 test), and heat it over a Bunsen lamp. The salt first dissolves in its 'crystal water,' which, however, is soon driven off, when the anhydrous salt remains as a solid mass. On further heating, this solid melts, but up to about 300° C.† it undergoes no chemical change. At a red-

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* To insure the presence of a *moderate* excess, use a standardised acid, and calculate the quantity required, as if the salt to be decomposed were carbonate, Na_2CO_3.

† This high degree of stability is characteristic of alkaline *acetates*; the alkaline salts of most other organic acids are decomposed at such a high temperature.

heat the salt is slowly decomposed with formation of carbonate, but without blackening.

After having verified these statements, add to the fused salt a fragment of caustic potash or soda; flames of marsh-gas, CH_4, burst forth from the mass.

199. Heat some *acetate of lime* in a hard glass tube to dull redness. It is decomposed into aceton vapour which escapes, and *carbonate of lime* which remains. No charcoal is formed. Identify the carbonate. Give the equations of the reactions referred to in sects. 198 and 199.

200. Take specimens of dilute acetic acid (or of the distillate produced in exercise, sect. 196), and subject them severally to the following operations:

201. (A) Add some dilute sulphuric acid, and one drop of *bichromate of potash*, and heat the mixture for, say, half an hour in a (boiling) water-bath. There is no change in either the acid or the reagent.*

A similar negative result is obtained when permanganate of potash is substituted for the chromate.

202. (B) Boil with precipitated *oxide of mercury* for a while, and filter. The filtrate contains mercuric acetate.

203. (C) Add some drops of *nitrate of silver*, and heat. There is no visible change.

204. (D) Neutralise cautiously with (say) baryta water; add nitrate of silver, and heat. Acetate of silver *may* come down on cooling as a crystalline precipitate; but in no case is the silver salt *reduced* to metal.

205. (E) Neutralise with a convenient base, and evaporate to a small volume (or take a strong solution of, say, ready-made acetate of soda); add one volume of concentrated sulphuric acid and some alcohol, and heat. Acetic ether vapour is evolved, which exhibits a characteristic agreeable smell.

206. *Note.*—Acetic acid is the second term in a large homologous series of acids of the general formula, $C_nH_{2n}O_2$ or $(C_mH_{2m}+_1)COOH$, called fatty acids.

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* Holds for a 'large minority' of organic acids. Most organic acids are oxidised by the CrO_3, which, by loss of oxygen, is reduced to (green) chromic salt.

Any two or three successive terms of this series are in general very similar, so that it is difficult to distinguish them from one another. This, however, does not hold for the first two terms, as will be seen by the following exercises on

FORMIC ACID, H . COOH.

207. Heat some formate of lime in a hard glass tube over a Bunsen. The salt is decomposed with formation of the aldehyde CH_2O, which escapes, and of a residue of pure (charcoal-fire) carbonate.

208. Heat some of the same salt (or any other formate) with 60 per cent. sulphuric acid in a test-tube, provided with a gas-evolution tube. The salt is decomposed with evolution of pure *carbonic oxide*, a colourless gas, which, when kindled, burns with a *blue* flame into carbonic acid. There is *no* charcoal formed, the liberated acid being simply dehydrated by the vitriol, and reduced to $CO = CH_2O_2 - H_2O$.

Verify the following statements, and contrast the results with those of the corresponding experiments on acetic acid:

209. Aqueous formic acid, when boiled with (precipitated) *oxide of mercury*, gives off carbonic acid with formation of a black precipitate of metallic mercury.

210. When a solution of formic acid or of a formate is mixed with *nitrate of silver*, a white precipitate of formate of silver *may* be produced; but in any case the mixture, when heated, gives a black precipitate of metallic silver, with evolution of CO_2, according to equation:

$$CH_2O_2 + Ag_2O = Ag_2 + H_2O + CO_2.$$

211. A solution of formic acid, when mixed with *chloride of platinum* and an excess of carbonate of *soda*,* deposits, on boiling, a black precipitate of metallic platinum, the formate being oxidised into carbonate.

212. The aqueous acid, when heated with carbonate (or

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* Not potash, which would produce a precipitate of $PtCl_6K_2$.

oxide) of lead, dissolves the oxide, and the filtered liquid (if not too dilute) deposits, on cooling, sparingly soluble crystals of the salt $(CHO_2)_2Pb$.

TARTARIC ACID.

(Recapitulate sects. 192 to 194, and then continue, as follows):

213. Neutralise a (say, 5-per-cent.) solution of *tartaric acid* with one of caustic potash. The liquid now contains the normal potassic tartrate, which, being very soluble, remains dissolved.

214. To the neutral liquid produced, add a quantity of tartaric acid solution, and stir with a glass rod. An abundant crystalline precipitate of the 'bitartrate,' $C_4H_5KO_6$ ('cream-of-tartar') is formed. The precipitate dissolves readily on addition of excess of caustic potash (or $NaHO$, or NH_4HO); or of hydrochloric (sulphuric or nitric), but it is not materially attacked by moderate quantities of *acetic, acid.* After having verified these statements,

215. Neutralise some of the tartaric acid solution with caustic soda; then acidify with acetic acid; and after having satisfied yourself that the solution remains clear, add a little of a concentrated solution of acetate of potash, and stir. A precipitate of cream-of-tartar soon makes its appearance.

216. To a solution of tartaric acid, add excess of *lime-water:* a precipitate of tartrate of lime is produced.

217. To a solution of normal alkaline tartrate (say, Rochelle salt), add one of *chloride of calcium* as long as a precipitate is formed. The precipitate is identical with the one obtained in sect. 216. Collect the lime-salt on a filter, wash it with water, and then boil it in a basin with a solution of carbonate of potash for about five minutes, to convert the lime-salt into a solution of the normal potash salt. Filter off the carbonate of lime, acidify the filtrate by means of acetic acid, and stir. Bitartrate of potash is produced, and comes down as a precipitate—more readily on addition of alcohol.

218. Mix 1 grm. of cream-of-tartar, 1·6 grm. of oxide of antimony (Sb_2O_3), and 30 c.c. of water in a basin, and

boil the mixture for about a quarter of an hour (replacing from time to time the vaporised water), and then filter off what is left undissolved. The filtrate is a solution of *tartar-emetic*, which, by evaporating the solution to a small enough volume, and allowing it to cool, may be obtained in crystals (of the composition $C_4H_4O_6\left\{\begin{matrix}K\\SbO\end{matrix}\right. + \frac{1}{2}\,H_2O$). In this reaction, the Sb_2O_3 behaves as if it were a monoxide $(Sb_2O_2)O$, combining, under the circumstances, with H_2O into a *basic* hydrate $(Sb_2O_2)O + H_2O = 2(SbO)OH$, analogous to KOH. From these data deduce the equation of the reaction.

219. To some of your tartar-emetic solution add hydrochloric acid, drop by drop: a precipitate of SbOCl is produced, which, however, dissolves in excess of the acid.

220. To another portion add *sulphuretted hydrogen* in excess (without HCl). The antimony is completely precipitated as sulphide, Sb_2S_3. What is in the filtrate? Verify your answer experimentally.

CITRIC ACID, $C_3H_5O\,.\,(COOH)_3$.

221. Procure a specimen of citric-acid crystals, and observe their general properties and their behaviour (*a*) when heated by themselves; (*b*) when heated with oil of vitriol. Then dissolve some of the acid in about twenty times its weight of water, and use the solution for the following tests, always contrasting the results with those obtained under similar circumstances with tartaric acid:

222. To some of the solution add excess of *lime-water;* the solution remains clear; on long-continued boiling, citrate of lime is precipitated.

223. Take another portion, and neutralise it by very gradual addition of caustic potash. *No* precipitate is formed at any stage of the process.

224. Take another portion, neutralise it with caustic soda or potash, and add *chloride of calcium:* a precipitate of citrate of lime is produced. Collect and wash the precipitate, and subject it to the operation described in sect. 217

for obtaining a cream-of-tartar precipitate from tartrate of lime. The result will be negative.

SUCCINIC ACID, $C_2H_4 . (COOH)_2$.

225. Procure a specimen of the crystallised acid, observe the appearance of the crystals and their behaviour to water in the cold and in the heat, and report.

226. Heat a few crystals cautiously over a Bunsen in a dry test-tube. The acid sublimes—part of it as anhydride, $C_4H_4O_3$—*without charring*.

227. Heat another specimen with *oil of vitriol:* the acid dissolves without charring or gas-evolution.

Dissolve 1 grm. of the acid in about 50 grms. of water, and use separate portions of the solution for the following experiments:

228. (A) Add some dilute sulphuric acid and a drop of *permanganate of potash* solution. There is no visible change, not even on boiling.

229. (B) Supersaturate with pure *caustic soda*, and colour with permanganate. There is no change in the cold; on heating, the mixture (which is at first red) slowly assumes a violet tinge, indicating a gradual but slow oxidation of the acid.

230. (C) Neutralise with ammonia, and add *ferric chloride:* the acid is precipitated in the form of a brownish red ferric salt.

BENZOIC ACID, $C_6H_5 . (COOH)$.

Procure a specimen of crystallised acid, and examine it in a general way.[*] Then

231. Heat some of the acid in a dry test-tube over a Bunsen. The acid fuses (at 121° C.), and gradually sublimes without residue; the sublimate forms slender silky-white needles. The vapours have a peculiar smell.

232. Mix one part of benzoic acid with about 25 parts, by weight, of cold water: the acid does not dissolve visibly. Now heat to boiling: the acid does dissolve, but on cooling

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[*] Observe that the pure acid has no smell. The pleasant odour observed in the Pharmacopœia acid is owing to an impurity.

it separates out again almost completely, as it requires about 600 times its weight of cold water for solution.

233. To the magma of benzoic acid and water obtained in the last exercise, add caustic soda, drop by drop, to produce a (slightly alkaline) solution of benzoate of soda. Use separate quantities of the solution for the following tests :

234. (A) Acidify with hydrochloric acid : a precipitate of benzoic acid is formed. (Tartaric, citric, succinic acid, when thus liberated, remain dissolved.)

(B) Add a solution of ferric chloride, previously mixed with as much ammonia as can be added without producing a permanent precipitate. The acid is precipitated as a voluminous pale-red basic ferric salt.

The general student may break off here ; the following Appendix being added chiefly for the benefit of *medical students.*

APPENDIX.

ALKALOIDS.

235. This term is customarily applied to the nitrogenous bases of the vegetable kingdom. These may be divided into two classes, namely:

(1) *The Non-oxygenated Bases.*—All volatile liquids of the elementary composition, $C_xH_yN_z$, insoluble or slightly soluble in water, but soluble in ether. All more or less closely allied to ammonia in their chemical character. Examples: Nicotine, the alkaloid of tobacco; conia, the alkaloid of hemlock.

(2) *Oxygenated Bases.*—These all contain oxygen besides C, H, N. They are less closely allied than the first class to ammonia. The free bases generally are crystalline solids, insoluble or sparingly soluble in water, but more readily soluble as a rule in alcohol, ether, chloroform. They are all soluble in aqueous mineral (and many organic) acids, forming salts. To become acquainted with some of the

General Methods

for the detection of alkaloids as a class of bodies, the student may practise the following exercises with, say, a solution of *sulphate of quinine*, as obtained by shaking the commercial sulphate with 100 times its weight of water and adding sulphuric acid, drop by drop, until a clear solution is produced.

(*To separate portions of this solution add*)

236. (A) *Caustic potash* or soda. The alkaloid is almost completely precipitated; the precipitate is insoluble in excess of the alkali. Many other oxygenated alkaloids behave similarly, except that some, for example morphia, do dissolve in an excess of reagent.

237. Collect the precipitate (best produced with caustic *soda*) on a filter, wash it with small instalments of cold water, dissolve it in a little water acidulated by hydrochloric acid, add chloride of platinum, evaporate on a water-bath to a small volume and add alcohol: a yellow precipitate not unlike in appearance, and closely analogous in constitution, to chloroplatinate of ammonium is produced. All alkaloids form such chloroplatinates, but the solubilities of these vary very much from one species to the other.

238. (B) Add a solution of *iodine in aqueous iodide of potassium.* A flocculent brown precipitate is formed which contains the alkaloid in the form of a polyiodide (compound of hydriodate with extra iodine).

(C) Add solution of the double salt, $HgI_2 + 2KI$: the quinine is completely precipitated in combination with mercuric iodide.

(D) Add solution of *phospho-molybdic acid:* the alkaloid is precipitated in the form of a yellow phospho-molybdate, analogous in constitution to the well-known yellow ammonia compound obtained in testing for phosphoric acid with molybdate of ammonia. The precipitate is almost insoluble in all ordinary dilute acids, except phosphoric. It can be washed without loss with very dilute nitric acid mixed with some of the reagent. After having thus washed your precipitate, treat it with carbonate of potash solution: it dissolves with liberation of quinine, which *may* appear as a precipitate, but—whether or no—can be extracted from the mixture by shaking it with ether. The ethereal layer, when allowed to evaporate spontaneously, furnishes crystals of the alkaloid.

(E) Add solution of *meta-tungstic acid:* the alkaloid is precipitated as a meta-tungstate. This is a perfectly general and very delicate reaction. From the washed precipitate the alkaloid can be eliminated by treatment with baryta-water, and isolated by distillation, if it is a volatile one, or by shaking the mixture with ether or chloroform.

Reactions B, C, D, E apply to all alkaloids without exception.

Special Tests for the Identification of Individual Alkaloids.

239. **Quinine.**—(Use a solution of the commercial sulphate in water acidulated with sulphuric acid.) This solution exhibits blue fluorescence. The precipitate produced in it by addition of ammonia dissolves when the mixture is shaken with ether. (This distinguishes quinine from cinchonine.)

The solution when mixed, first with chlorine water and then with ammonia, strikes an intense green colour.

240. **Morphia.**—The free alkaloid is *insoluble* in ether; most alkaloids are soluble in this menstruum.

To a solution of the muriate add, drop by drop, caustic potash: the precipitate of morphia first produced dissolves in excess of reagent. (Most other alkaloids are insoluble in alkalies.)

To other two separate portions add (*a*) neutral ferric chloride, (*b*) iodic acid. The (*a*) mixture assumes a blue, the (*b*) a brown colour; this brown colour is partially due to the presence of free iodine, which is readily identified by means of starch or bisulphide of carbon.

241. **Strychnine.**—Solutions of this alkaloid have a bitter taste of characteristically great intensity and persistence.

Dissolve a few milligrams of strychnine or strychnine salt in a few drops of oil of vitriol on a watch-glass, and to the colourless solution produced add a granule of bichromate of potash: there appears a most intense violet colour, which after some time passes into yellowish-red.

From solutions containing as little as 1 grm. of strychnine per litre, the alkaloid is precipitated (on standing for a night) by chromate of potash. The dry chromate when dissolved in oil of vitriol gives the characteristic colour mentioned before.

242. To practise

Stas' Method for extracting Alkaloids from Organic Mixtures.

Mix, say, 2 centigrams of strychnine with 50 grammes of minced meat. Then (in order to extract the alkaloid) digest the mixture in 200 c.c. of alcohol, acidified with tartaric acid, on a water-bath, filter, and wash with warm alcohol. Concentrate the filtrate on a (merely simmering) water-bath until the bulk of the alcohol is gone, and remove the fat which will have separated out, by filtration through a water-wet filter. Evaporate the filtrate at a temperature not exceeding 50° C to the consistence of an extract, which then exhaust with absolute alcohol. Filter the alcoholic liquor, evaporate to dryness (below 50°), take up the residue with water, filter again, if necessary, and shake with *chloroform.* The chloroform removes fats and other matter, but does not touch the alkaloid as long as it is present as *an acid-salt solution.* After removing the chloroform layer, add excess of caustic potash, and shake with fresh chloroform. This time the chloroform extracts the alkaloid, which separates out in the solid form when the chloroform is allowed to evaporate (spontaneously). The residual strychnine is pure enough to be identified by the tests given above.

EXPERIMENTS ON SOME OF THE SUGARS.

243. Procure specimens of

(A) White sugar-candy and loaf-sugar, either of which may be accepted as pure cane-sugar, $C_{12}H_{22}O_{11}$.

(B) Best commercial *grape-sugar*—as an apology for *dextrose*, $C_6H_{12}O_6$.

(C) *Milk-sugar* in crystals; $C_{12}H_{22}O_{11} . H_2O$.

And after having compared them in regard to their general appearance, crystalline form, and taste, grind up a portion of each in a mortar, and observe the behaviour of the powder when treated gradually with more and more of cold water. The solutions obtained should be diluted with water to about twenty times the weight of substance, and kept for the tests to be given presently. But before doing these tests, take separate quantities of (powdered) A, B, C, make each into a paste by addition of a little water, and add 3—4 volumes of oil of vitriol, and see what takes place. Report on, and remember, your observations. In order now to learn to discriminate between cane-sugar on the one hand, and the *glucoses*, $C_6H_{12}O_6$, on the other, verify the following statements with solutions of cane-sugar and grape-sugar respectively :

<table>
<tr><th rowspan="2">Reagent.</th><th colspan="2">Reactions of</th></tr>
<tr><th>Cane-sugar.</th><th>Glucose—
for example, grape-sugar.</th></tr>
<tr><td rowspan="2">Caustic potash or soda.</td><td colspan="2">The alkali combines with the sugar into a solution of a saccharate, which</td></tr>
<tr><td>is stable even in the heat.</td><td>when allowed to stand, and quickly on heating, is decomposed, with formation of in-intensely brown substances.</td></tr>
<tr><td>Dilute sulphuric or hydrochloric acid.</td><td>When boiled with the reagent, breaks up into dextrose and levulose (‘invert-sugar’).</td><td>No change even on boiling.</td></tr>
<tr><td rowspan="2">‘Fehling’s solution.’ *</td><td colspan="2">To a given volume of Fehling’s solution add about four volumes of water, and then a few drops of the sugar solution. Allow first to act in the cold, and then heat to boiling.</td></tr>
<tr><td>The mixture remains unchanged in the cold. In the heat there is a slight turbidity caused by Cu_2O formed.</td><td>The glucose is oxidised slowly in the cold, quickly on heating, with formation of a red precipitate of cuprous oxide.</td></tr>
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* Dissolve 34·65 grms. of sulphate of copper, $CuSO_45H_2O$; 173 grms. of Rochelle salt, and 70 grms. of caustic soda in water, mix and dilute to 1 litre. The blue liquid produced is capable of oxidising 5 grms. of glucose.

Fehling's test is a most delicate indicator of glucose and *milk-sugar*. After having tried it with the two solutions named, and with milk-sugar, apply it to the solution of 'invert-sugar' produced in the previous experiment, taking care first to saturate the acid with caustic alkali.

STARCH.

244. By means of a razor prepare a very thin slice of the inner substance of a potato, and look at it under the microscope, using a power of, say, 300 diameters. Do the same with minute specimens of flour of, say, wheat, maize, rice, and with arrowroot. You will have no difficulty in seeing the starch granules contained in these materials. Moisten each of the specimens with a drop of a dilute solution of *iodine* in iodide of potassium, and place them again under the microscope. The starch granules now have an intensely blue colour, and thus are more readily distinguished from the substances accompanying them.

To extract Starch from Wheat Flour.—Work it up with water into a stiff dough, which knead in your hand under a thin stream of water. Most of the starch runs away with the water as part of a milky liquid, which deposits its starch on standing in the shape of a heavy, pasty precipitate. The *gluten* (a mixture of albuminoids) remains as a sticky, tenacious mass. Wash your starch precipitate with cold water by decantation, and use it for verifying the following statements :

Starch is insoluble in (even boiling) ether or strong alcohol. It is insoluble in cold water, even when this is mixed with a little mineral acid or caustic alkali. In the case of alkalinised water, any albuminoids that may be present pass into solution, and can be precipitated by acidification.

When heated with about 10 parts of water to 70° or higher, it unites with the water into semi-transparent colloidal hydrate which, on cooling, sets into a jelly (starch paste). The paste readily mixes with additional water, especially in the heat. To a thin starch 'solution' add a drop of *iodine solution:* the mixture becomes intensely blue. The colour disappears on heating, but comes back on cooling.

To another portion of a (not too thick) starch paste add about 5 per cent. of aqueous hydrochloric acid,* and boil in a basin, until a drop, when taken out and mixed with iodine solution, no longer strikes a blue colour. The solution now is one of dextrine, $C_6H_{10}O_5$, and dextrose, $C_6H_{12}O_6$. Mix some of this solution with alcohol: the dextrine is precipitated; the dextrose remains dissolved. Filter, evaporate off the alcohol, and apply Fehling's test.

EXPERIMENTS ON URINE.

245. Procure a specimen of healthy urine, observe its smell, colour, action on test-papers. Determine its specific gravity (at 15° C.). Report results.

246. To separate out the *uric acid*, add to say 100 c.c. of the urine 5 c.c. of ordinary hydrochloric acid, and allow to stand overnight. Collect the uric-acid precipitate on a filter, and wash it with water. To identify it, dissolve a little of the dried precipitate in a few drops of nitric acid on a watch-glass, evaporate to dryness at a *gentle* heat, and expose the residue to ammonia vapours. The residue (if it does not already possess it) now assumes the intensely violet colour of murexide.

247. To isolate the *urea*, concentrate some of the urine by evaporation over a water-bath to about one-third of its original volume; allow to *cool*, and add 1—2 volumes of pure nitric acid of 1·4 specific gravity. The urea is transformed into nitrate, $CON_2H_4 . HNO_3$, which separates out gradually in crystals. Collect the crystals on a funnel stopped with glass-wool, wash them with small instalments of cold dilute nitric acid, dry them on a porous plate.

248. Dissolve some nitrate of urea (or pure urea) in water, add *nitrite of potash* and some *nitric acid:* the urea is decomposed with evolution of nitrogen and carbonic

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* H_2SO_4 has the same effect, but acts more slowly.

acid. Prove the presence of CO_2 in the gas by the lime-water test.

249. Dissolve some nitrate of (or pure) urea in water, add *mercuric nitrate* and enough of baryta-water to produce a neutral mixture. The urea is precipitated in the form of a white compound of mercuric oxide and urea.

250. To a solution of pure urea add one of *hypobromite of soda:*[*] the urea is decomposed quickly with formation of CO_2 and H_2O, which remain in the solution (the former as soda salt), and of nitrogen gas which escapes, in accordance, so far, with the equations: $CON_2H_4 + 3NaBrO = 3NaBr + CO_2 + 2H_2O + N_2$ and $CO_2 + 2NaHO = H_2O + Na_2CO_3$. This reaction readily lends itself to the approximate determination of the richness of a given sample of urine in urea.

251. To practise this method, take a flask of about 100 c.c. capacity, provide it with a well-fitting perforated india-rubber 'cork,' and, by means of a short glass tube passing through the perforation and a piece of capillary india-rubber tubing attached to the glass tube, connect the cork with a 'Mohr's Burette' turned upside down in a tall cylinder. To execute an analysis, charge the flask with 25 c.c. of hypobromite, and then place in it a short test-tube charged with (exactly measured) 5 c.c. of the urine to be tested, taking care that the urine meanwhile does not come into contact with the reagent. Immerse the flask up to the neck in a beaker charged with water of the temperature of the laboratory. On the other hand, fill the cylinder in which the burette stands with water (of the same temperature), so that, when now the upper end of the burette is connected with the flask, the water in the latter stands near the top mark. Adjust matters so that after equilibrium of temperature has been established, the water in the burette is at a level with that in the cylinder outside, and consequently the pressure of the air inside equal to that of the atmosphere, as measured by the height of the barometer. Now incline the flask so that the urine and the reagent mix and allow

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[*] 100 grammes of caustic soda are dissolved in 250 c.c. of water, and the (cold) solution is mixed with 22 c.c. of bromine.

the reaction to take its course, taking care to lift the burette higher and higher as the nitrogen gas comes off, so as to maintain the original pressure within the apparatus. When the gas-volume no longer increases, *re-establish the original temperature* and pressure*, and read off the level of the water in the burette. The difference between this reading and the one made on starting, gives the volume of the nitrogen evolved. Supposing this volume to amount to V c.c. at t° C. the barometer standing at B mm.; then taking τ as the numerical value of the tension of vapour of water at t°, we have, for the pressure P of the nitrogen, as it would be if, *without changing the volume V*, the vapour of water in it were removed, the value $P = B - \tau$; and for the absolute temperature the number $T = 273 + t$; hence the volume of the dry nitrogen at the absolute temperature $T = 1^\circ$, and the pressure $P = 1$ mm. would be

$$V_o = \frac{V \times (B - \tau)}{273 + t}.$$

But under these conditions, 1 c.c. of hydrogen (H_2) gas weighs ·0321 milligrams; hence 1 c.c. of nitrogen ($N_2 = 28$) weighs $\cdot 0321 \times \frac{N_2}{H_2} = \cdot 0321 \times 14$. But $N_2 = 28$ parts of nitrogen are contained in $CON_2H_4 = 60$ parts of urea; hence the weight of urea present in the sample of urine operated upon is W, and

$$W = \frac{V \times (B - \tau)}{(273 + t)} \times \cdot 0321 \times 30 \text{ mgms.};$$

and consequently, if 'U' c.c. of urine were operated upon, we have for the number of grammes of urea present in every litre of urine analysed, the equation,

$$x = \frac{V}{U} \times \frac{(B - \tau)}{(273 + t)} \times \cdot 963.$$

So we should say, if the equation given above were a correct theory of the process; but it is not, experiments of *Dupré's* having shewn that only 91 per cent. of the nitrogen of the urea is actually liberated. Hence the correct formula is:

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* This holds more especially for the water in the beaker, because, obviously, a slight increase or decrease of temperature there will cause a considerable change of total gas-volume.

$$x = \frac{V}{U} \times \frac{(B - \tau)}{273 + t} \times 1{\cdot}058.$$

When a long series of urea determinations has to be made, it is worth while to reduce the trouble involved in the computation of this formula to a minimum, by so modifying the method as to give both to B (that is, the pressure of the moist gas), and also to t constant values. If, for instance, we take care always to make $B = 760$ mm. and $t = 15^\circ{\cdot}5$ (= 60° F.), τ assumes the constant value of 13 mm., and we have

$$x = \frac{V}{U} \times 2{\cdot}74.$$

This latter equation will be readily understood by even those of our readers who have not yet learned to execute gasometric calculations, as it is only a symbolic expression for saying that (under the circumstances defined, and as a matter of experiment), to evolve 1 c.c. [1 litre] of nitrogen, we must have exactly 2·74 milligrams [grammes] of urea.

It is equally plain that, when we measure off exactly 2·74 c.c. of urine for each analysis, we always have

$$x = V \text{ numerically}$$

—that is, the volume of the nitrogen gives the number of grammes of urea per litre.

Diseased as contrasted with Normal Urine.

The following notes, although not pretending to give full instruction, may serve as a guide in the examination of a presumably morbid urine for clinical purposes.

252. *The* **Smell** of *normal* urine, though subject to variations, is never actually nauseous. A *putrid* smell (which is generally accompanied by an alkaline reaction) constitutes a pathologic symptom. Observe that *all* urine becomes putrid (and alkaline) on standing—except diabetic urine, which ferments like other glucose solutions.

253. *The* **Colour** of *normal* urine varies from straw- to amber-yellow. In certain diseases the urine is intensely yellow, yellowish red, brown, or even black. An abnormal colour may be owing to *biliary* matter, which is discoverable by the following (*Pettenkofer's*) test: [Remove the albumen, if present] Add a drop of dilute *sulphuric acid*, and a trace of cane-sugar, and evaporate at a gentle heat; the cholalic acid present in the bile will cause a violet or red coloration. —It is as well here to add that very abnormal colours may be produced in healthy urine by the internal administration of certain drugs, such as *rhubarb*, *senna*, *logwood*, *santonine*.

254. **Action on Test-Papers.**—*Normal* urine as a rule colours blue litmus-paper red; sometimes it is neutral. An alkaline reaction very rarely presents itself, and, if it does, is owing to *fixed* alkali. An alkaline reaction in fresh urine caused by *carbonate of ammonia* is a morbid symptom (compare sect. 252). To test an alkaline urine for carbonate of ammonia, evaporate it in a basin over a water-bath; the alkaline reaction soon disappears.

255. **Relative Clearness.**—*Normal* urine as voided is *clear*; but on standing for some hours it deposits a cloud of *epithelial scales* from mucous membranes. Other *organised* deposits hardly ever occur under normal conditions; although non-organised precipitates often appear on standing. In *diseased* urine, deposits are of frequent occurrence, and sometimes a precipitate is present even from the first.

256. The following is a list of the more frequent *components of urinary deposits*:

(1) *Phosphate of Lime*, $Ca_3P_2O_8+xAq$.—Always amorphous. Non-combustible. Soluble in acetic acid; solution is precipitated by oxalic acid. Nitric solution of ash gives the molybdenum test for P_2O_5 (sect. 72).

(2) '*Triple Phosphate*,' $Mg.NH_4.PO_4+6H_2O$.—When viewed microscopically, found to consist of distinct crystals. Non-combustible. Soluble in acetic acid; solution gives *no* precipitate with oxalic acid. Nitric solution gives the molybdenum test (sect. 72).

(3) *Oxalate of Lime*, $CaC_2O_4 + H_2O$.—When viewed microscopically, found to consist of crystals. Soluble in hydrochloric, but *insoluble in acetic acid.* Ash consists of pure CaO or $CaCO_3$.

(4) *Uric Acid*, $C_5H_4N_4O_3$, forms generally a reddish precipitate, consisting of microscopic crystals. Insoluble in hydrochloric acid. Recognisable by murexide reaction given in sect. 246.

(5) *Urates* of soda, ammonia, potash, appear sometimes as amorphous, sometimes as crystalline precipitates. The former (which are very common) dissolve when the urine is gently warmed. Hydrochloric acid eliminates (a precipitate of) uric acid.

(6) *Cystine*, $C_3H_7NSO_2$.*—Microscopic crystals, generally of the form of hexagonal plates. Insoluble in acetic acid, but soluble in ammonia, from which it separates out, on spontaneous evaporation, in magnificent lustrous plates. When fused with caustic potash on (cupriferous) silver foil, it produces a black stain of metallic sulphide.

Of organised deposits we may mention :

(7) *Casts of uriniferous tubes.*

(8) *Blood corpuscles.*

(9) *Pus corpuscles.*

These (7, 8 and 9 ; also 10) occur only in *morbid* urines ; they can be recognised under the microscope. Occasionally

(10) *Fat globules* make their appearance. These do *not* settle ; they are easily extracted by shaking with *ether.* The ethereal layer, when allowed to evaporate spontaneously, leaves the fat.

257. To examine a urine deposit, allow the urine to stand in a conical test-glass ; wait until the precipitate has settled ; and next, by means of a pipette, lift out a portion of the lowest turbid stratum, of which place a small sample under the microscope. With some practice, there is no difficulty in discriminating between *amorphous*, *crystalline*, and *organised* things, and after *considerable experience with well-authenticated specimens*, it is possible even, to some extent, to recognise the several individual things above named by their morphologic characters. After having done so as far as possible, treat separate portions of the magma

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* Occurs very rarely and only in certain diseases.

with acetic acid, hydrochloric acid, ammonia; again apply the microscope, and interpret your observations. When there is a sufficient quantity of material, collect it on a filter, wash it with cold water, and apply to it the ordinary methods of analysis.

258. *Degree of Concentration.*—In normal urine, the specific gravity (as referred to water = 1000) ranges from 1015 to 1025; but it occasionally rises as high as 1036.* Approximately, the excess of the specific gravity over 1000, multiplied by 2, gives the number of grammes of solids per litre; thus, for instance, the density 1036 corresponds to 2 × 36 = 72 grammes of solids per litre. Of these, in normal urine, one-half about consists of urea, the rest of chlorides, sulphates, phosphates of the bases K_2O, Na_2O,CaO, MgO; of uric acid, urates, and numerous minor organic components. Compared with the ratio of total solids to water, the quantitative composition of the solids is *relatively* constant. Hence a high specific gravity, in general, indicates a high percentage of urea; sometimes it is so high, that nitric acid, when added to the plain urine, precipitates the urea as nitrate (comp. sect. 247). A high specific gravity, combined with a very light colour and comparative absence of smell, indicates *sugar*.

259. Of *abnormal dissolved* constituents, *dextrose* and *albumen* are the most important. Neither of them ever occurs in healthy urine, hence their presence always proves a diseased condition of the system.

260. The detection of **sugar** is easily effected by means of the tests given in the table, sect. 243, to which we will add the following as being particularly handy for medical practitioners: Add to the suspected urine a few drops of *carbonate of potash* solution, and a pinch of ordinary *trisnitrate of bismuth*, and heat to boiling. In the presence of the least trace of sugar, the originally white precipitate assumes a brown or black colour. Before applying this test, one should make sure of the absence of

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* Roberts's *Practical Treatise on Urinary, &c. Diseases.*

sulphuretted hydrogen, but this substance occurs in urine only in the rare case of *cystosis*.

261. **Albumen.**—To test for albumen, make sure that the urine is *not alkaline;* if it is, neutralise it with acetic acid. Heat to boiling. A coagulum formed consists of *albumen* or earthy phosphates. To discriminate between these, add a few drops of *nitric acid;* the phosphates dissolve, the albumen remains. Or shortly: heat to boiling, and acidify strongly with nitric acid. A *permanent* precipitate is sure to consist of albumen.

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